



2,2,4,4-Tetrathio substituted 1,3-dithietanes

Wolfgang Weber*, Helen Chirowodza, Harald Pasch

Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa



ARTICLE INFO

Article history:

Received 24 August 2012

Received in revised form 13 December 2012

Accepted 21 December 2012

Available online 29 December 2012

Keywords:

Thiophosgene

Carbonotrithioates

1,3-Dithietanes

Tetrafunctional RAFT agent

ABSTRACT

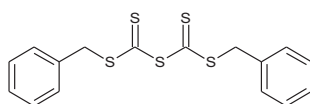
The synthesis of 2,2,4,4-tetrathio substituted 1,3-dithietanes and their intermediates by reaction of thiophosgene with carbonotrithioates or *O*-ethylthiocarbonate is reported. Their reactivity against thermolysis and aminolysis was investigated.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The reaction of alkyl mercaptides with carbon disulfide to alkyl carbonotrithioates, followed by alkylation, is commonly used to prepare unsymmetrical dialkyl carbonotrithioates,^{1,2} which can act as RAFT agents in controlled polymerization reactions of styrene and other monomers.^{3,4}

In 2008 an extended structure to the carbonotrithioates with an additional –S–CS– functionality was reported with the synthesis of the red colored pentathiodicarbonates⁵ (Fig. 1).



dibenzyl pentathiodicarbonate

Fig. 1. Chemical structure of dibenzyl pentathiodicarbonate.

In continuation of that work we recently investigated if the sulfur containing part of those compounds can be extended further by joining two carbonotrithioates with the reactive thiophosgene to form a thiocarbonyl bridge. The resulting substance should contain seven sulfur atoms and be intensely colored.

* Corresponding author. Tel.: +27 (21) 808 3176; fax: + 27 (21) 808 4967; e-mail address: wgweber@sun.ac.za (W. Weber).

2. Results and discussion

Benzyl mercaptan was therefore reacted with carbon disulfide in the presence of aqueous potassium hydroxide to afford the potassium salt of benzyl carbonotrithioate **1a**. Addition of thiophosgene resulted in a yellow solid, which was isolated and characterized. For such a conjugated structure we expected a red or purple colored compound, not a yellow product. The ¹³C NMR spectrum in carbon disulfide contains only a signal for one thiocarbonyl group at 217.99 ppm, not for two with different values as expected for **2a**. The product, which is insoluble in most organic solvents, was crystallized from carbon disulfide and its crystal structure determined by X-ray diffractometry. The results show clearly that the compound is a dimer of the envisaged compound **2a** and contains a 1,3-dithietane ring in the central position. The ¹³C NMR spectra of **3a** and **3b** contain further proof of the formation of 1,3-dithietanes by displaying small signals for a quaternary carbon atom at 72.42 and 72.66 ppm, respectively, which is in good agreement with literature data.⁶

The four-membered 1,3-dithietane ring could be formed in two ways, the reaction of dimeric thiophosgene (2,2,4,4-tetrachloro-1,3-dithietane) with potassium benzyl carbonotrithioate or by dimerization of the relevant thioketone⁷ under the selected reaction conditions.

The first pathway is not likely. Dimeric thiophosgene is primarily formed by UV radiation of thiophosgene^{8a–c} or by Lewis acid assisted dimerization.⁶ Both conditions were not encountered here.

Kato et al.⁷ reported that aliphatic thioanhydrides decompose easily at room temperature and result in 1,3-dithietanes and other

products. Upon comparing their thioanhydrides with our structures the pathway involving dimerization seems plausible. A further indication for that pathway is the appearance of a red color while adding thiophosgene to the trithiocarbonate salt and small quantities of remaining red oils in the mother liquor. The red color most probably originates from the intermediate dibenzyl heptathiotricarbonate **2a**.

Depending on the solvent system and mode of addition of thiophosgene, the yield of the product **3a** is between 30% and 65%. The highest yields of product are isolated if the reaction is carried out in water, thiophosgene added without a solvent and the black oily product stirred with THF to separate the yellow product from other more soluble by-products (Procedure B). At some stage we suspected, that the possible peroxide content in THF led to the isolation of the yellow dimer from the dark oil, but that could not be confirmed. Even after using purified and freshly distilled THF the dimer was formed. Solvents other than THF act similarly. A number of by-products are formed. If the thiophosgene is dissolved in THF and added dropwise, carbon disulfide is eliminated and dibenzyl disulfide **4**^{9a–c} (Fig. 2) can be isolated in a yield of 21%. Dissolving thiophosgene in carbon disulfide or chloroform also led to a decreased yield of **3a** (30–40%).

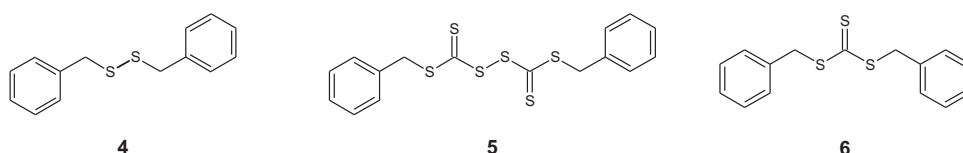


Fig. 2. Structures of **4**, **5**, and **6**.

To decrease the chances of by-product formation via hydrolysis, a different approach was taken. The potassium alkyl carbonotrithioates **1a** and **1b** were prepared beforehand and dry benzene used as solvent in the condensation step with thiophosgene, which led to slightly improved yields of 70% compared to the water based reaction (Procedure A). When the reaction was carried out in dry diethylether, **3a** was isolated in 65% yield. Stopping the reaction after 75 min afforded **3a** in 51% yield and a red oil as by-product. The oil contained several compounds, amongst them more of **3a** (12%) and the assumed intermediate dibenzyl heptathiotricarbonate **2a**. Column chromatography on silica with pentane/ethylacetate (2:1), followed by a second separation with pentane led to the isolation of **2a**. Other yellow products remained on the column under the conditions used. In contrast to the column purification of **7** we were not able to isolate pure dibenzyl heptathiotricarbonate **2a**. The NMR spectroscopic data of **2a** are reported in the Experimental section. All data are consistent with the proposed structure. The data for the unidentified impurity are omitted.

Compound **3a** is quite stable against hydrolysis. It does not react with 32% hydrochloric acid in carbon disulfide at room temperature. Stirring of **3a** in benzene with an excess of 5% sodium

hydroxide and one drop of Aliquat 336 led to a recovery rate of 58% **3a** after 2 days stirring at room temperature. 29% of dibenzyl disulfide **6** was also isolated and identified.

Furthermore, we also investigated the decomposition of **3a** in inert solvents under elevated temperatures. Two solvents were used under reflux conditions, bromobenzene (bp 156 °C) and chlorobenzene (bp 132 °C). The reaction products and their yields results were comparable. Heating **3a** in chlorobenzene leads to several red and yellow colored products, of which the two main components were identified after column chromatography as bis(benzylsulfanyl thiocarbonyl)disulfide **5**¹⁰ and dibenzyl trithiocarbonate **6**¹¹ (Fig. 2). Bis(benzylsulfanyl thiocarbonyl)disulfide **5** itself is stable under the reaction conditions (2 h reflux in chlorobenzene) and was fully recovered.

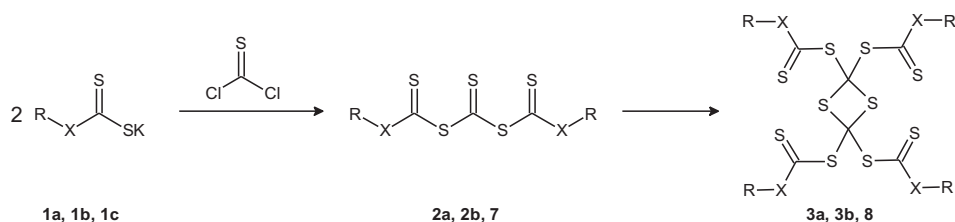
The prepared 1,3-dithietane **3a** was tested as a multi-arm RAFT agent in the polymerization reaction of styrene and other monomers and the results will be published separately in due course.

To be able to characterize the polystyrene chains, the sulfur containing end groups, originating from the RAFT agents, are preferably removed by aminolysis.

As a preliminary experiment **3a** was therefore treated with 4 or 5 mol-equiv of *n*-propylamine in THF. Within 15–20 min the solid **3a**

dissolved and the solution turned orange. The main product of that aminolysis was identified as dibenzyl disulfide **4** (Fig. 2), which was isolated in a yield of 78%. The residual orange oil contains several colorless, yellow and red products. Based on the small amount of the oil (1.25 g of 6.25 g possible as suggested by the desired structure) one has to assume that under the reaction conditions most of **3a** is decomposed further into small volatile molecules, such as carbon disulfide and propyl isothiocyanate, which were not recovered under the work-up conditions. Elemental sulfur is a further product and separates out of the THF solution.

Surprisingly, replacing one sulfur atom in the alkyl carbonotrithioates by oxygen (potassium *O*-ethylthiocarbonate instead of potassium ethoxy(thio)ethanethiolate) and then carrying out the reaction under similar conditions did not afford a 1,3-dithietane, but the originally targeted linear structure of *O,O'*-diethyl pentathiotricarbonate **7** as a dark red oil, as this color is expected from such a conjugated system (Scheme 1). The crude product decomposed rapidly at room temperature and therefore had to be purified as soon as possible. The ¹³C NMR spectrum in CDCl₃ of the purified **7** shows two signals at 202.97 ppm and 209.12 ppm for the two different C=S functionalities.



Scheme 1. Reaction pathway for **2**, **3**, **7**, and **8**.

Download English Version:

<https://daneshyari.com/en/article/5218734>

Download Persian Version:

<https://daneshyari.com/article/5218734>

[Daneshyari.com](https://daneshyari.com)