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

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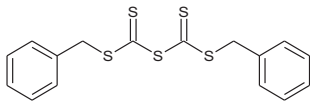
ABSTRACT

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

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 pentathiodicarbonates[5] (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.

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 ^{13}C 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 ^{13}C 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 thioketone[7] 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

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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 dibenzyldisulfide **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%).

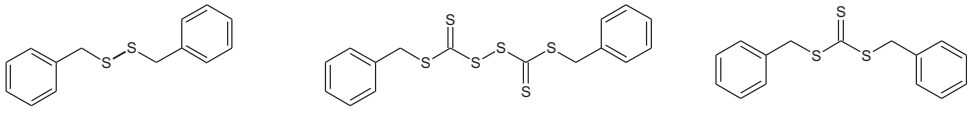
hydroxide and one drop of Aliquat 336 led to a recovery rate of 58% **3a** after 2 days stirring at room temperature. 29% of dibenzyldisulfide **6** was also isolated and identified.

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**



4 **5** **6**

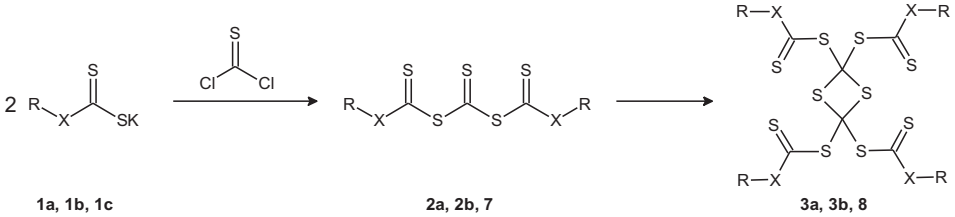
Fig. 2. Structures of **4**, **5**, and **6**.

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, amidst 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

dissolved and the solution turned orange. The main product of that aminolysis was identified as dibenzyldisulfide **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*-ethyldithiocarbonate instead of potassium ethoxy(thioxo)methanethiolate) 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 ^{13}C NMR spectrum in $CDCl_3$ of the purified **7** shows two signals at 202.97 ppm and 209.12 ppm for the two different C=S functionalities.



1a, 1b, 1c **2a, 2b, 7** **3a, 3b, 8**

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

Zbirovsky and Ettel[12] reported in 1957 the isolation of *O*,*O*′-dialkyl pentathiotricarbonates as dark red oils. In their case, thiophosgene was added to the potassium *O*-alkyl dithiocarbonate in benzene. Under basic conditions the oil is transformed into the dimeric structure with a melting point of 161 °C for alkyl=ethyl. When they changed the solvent system to diethylether, they isolated the dimeric structure in 89% yield. We modified their procedure and isolated the 1,3-dithietane **8** in 95% yield.

We identified the red oily *O*,*O*′-diethyl pentathiocarbonate **7** as by-product in the mother liquor. That compound decomposed overnight into a yellow, multi-component oil, which also contained traces of **8**. Synthetic procedures and spectroscopic data are given under the Experimental section.

The replacement of one sulfur atom (X=S) in the alkyl carbonotrithioates with nitrogen led to the formation of the dialkyldithiocarbamates, which react with thiophosgene to form different types of products by elimination of carbon disulfide, such as the dialkylthiuram monosulfides (*N*,*N*,*N*′,*N*′-tetraalkyldicarbono trithioic diamides).[12] The procedure was similar to the reaction of *O*-ethyldithiocarbonate with thiophosgene in benzene. The elimination of carbon disulfide as a side reaction also took place during the synthesis of **3a**, whereby dibenzyldisulfide **6** was formed (Table 1).

Table 1
Substituents in 1,3-dithietanes

Compound	R	X
1a, **2a**, **3a**	C_6H_5–CH_2–	S
1b, **2b**, **3b**	*n*-Bu	S
1c, **7**, **8**	Et	O

3. Conclusions

In the present study, we have demonstrated that sulfur-containing compounds can be extended further by joining two carbonotrithioates with the reactive thiophosgene to form a thiocarbonyl bridge. The resulting heptathiocarbonate dimerizes to form a heterocyclic sulfur compound (with a four-membered 1,3-dietane ring), which can be used as a RAFT agent.

4. Experimental

4.1. General remarks

All NMR spectra were acquired using a Varian VNMRS 300 MHz spectrometer. IR spectra were scanned neat using a Nicolet iS10 (Thermo Scientific) FTIR spectrophotometer (Transmission mode).

Caution: Thiophosgene and carbon disulfide are very dangerous chemicals and should be handled with extra caution in a well ventilated fumehood.

4.2. Reagents

Thiophosgene (Fluka, techn., 90% and 98%, respectively), potassium *O*-ethyldithiocarbonate **1c** (Merck) and sodium diethyl dithiocarbamate trihydrate (Aldrich) were used as received.

Potassium benzyl carbonotrithioate **1a** and potassium *n*-butyl carbonotrithioate **1b** were prepared by modifying a procedure described in literature.[13] The modification included using dry THF as solvent and a 1.05:1:1.25-ratio of KOH, mercaptan and CS_2. The potassium salts were isolated by removing the solvent under reduced pressure and dried under vacuum. The yields of **1a** and **1b** were 98% and 85%, respectively.

4.3. Experimental procedures

*4.3.1. Procedure A: synthesis of **3a** and **3b** in benzene*

*4.3.1.1. Tetrabenzyl(1,3-dithietane-2,2,4,4-tetrayl)tetracarbonotrithioate **3a**.* Potassium benzyl carbonotrithioate **1a** (4.75 g, 19.9 mmol) was suspended in dry benzene (40 mL) in a flask and stirred in ice-water. Thiophosgene (1.30 g, 11.3 mmol, 90%) in dry benzene (25 mL) was added dropwise over within 20 min. An intense red color developed and the solid dissolved. After stirring for a further 15 min, the cooling bath was removed and the mixture stirred overnight. The formed yellow solid was filtered off, washed several times with pentane until the solvent remained colorless, washed twice with water, and again with pentane. The yellow product, **3a** was dried at 50 °C (yield 2.55 g). Evaporation of the solvents afforded a red oil, which was treated with THF to result in a further 0.55 g of product. Yield: 3.10 g (70%) as yellow crystals, mp 160–161 °C. **3a** can be crystallized from carbon disulfide.

IR (neat) 3026, 2932, 1643, 1507, 1452, 1056, 816, 730, 696 cm^{-1}.

^1H NMR (300 MHz, CS_2, $CDCl_3$): δ (ppm) 7.26–7.20 (20H, m, Ar), 4.44 (8 H, s, CH_2).

^{13}C NMR (75.4 MHz, CS_2, $CDCl_3$): δ (ppm): 217.99 (C=S), 133.70, 129.16, 128.58, 127.75 (Ar), 72.42 (quart. C), 41.21 (CH_2).

Anal. calcd for $C_{34}H_{28}S_{14}+CS_2$ (961.66): C, 43.7%; H, 2.9%; S, 53.4%. Found: C, 43.8%; H, 3.0%; S 53.8%. **3a** contains one mol carbon disulfide if crystallized from CS_2.

The structure of **3a** was further confirmed by X-ray diffractometry.[14] The remaining oil consisted of several by-products, which were not characterized.

*4.3.1.2. Tetrabutyl(1,3-dithietane-2,2,4,4-tetrayl)tetracarbonotrithioate **3b**.* Thiophosgene (1.30 g, 11.3 mmol, ~90%) in dry benzene (25 mL) was added dropwise over 20 min to an ice-water cooled suspension of **1b** (4.10 g, 20.1 mmol) in dry benzene (40 mL). After a further 15 min the cooling bath was removed and the red solution stirred overnight at room temperature. The solvent was removed by evaporation and the red residue washed thoroughly with water. The solid was stirred in pentane (50 mL). The resulting yellow powder was isolated and washed with pentane and acetone until all red traces were gone. Concentration of the wash solvents led to a red, crystallizing oil, from which more product could be recovered by treatment with a few mL of pentane.

Yield: 2.45 g (66%) as yellow crystals, mp 126–127 °C ($CHCl_3$).

IR (neat) 2950, 2923, 2864, 1459, 1419, 1269, 1057, 820, 729 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.27 (8H, t, CH_2CH_2S, J=7.5 Hz), 1.66 (8H, quintet, CH_2CH_2S, J=7.5 Hz), 1.42 (8H, sextet, CH_3CH_2, J=7.5 Hz), 0.93 (12H, t, CH_3CH_2, J=7.5 Hz).

^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 220.03 (C=S), 72.66 (quart. C), 36.29 (CH_2), 29.84 (CH_2), 22.12 (CH_2), 13.57 (CH_3).

The residual oil contained several intense red or yellow by-products, which were not further identified.

*4.3.2. Procedure B: synthesis of **3a** in water*

*4.3.2.1. Synthesis of tetrabenzyl(1,3-dithietane-2,2,4,4-tetrayl) tetracarbonotrithioate **3a**.* Potassium hydroxide (7.30 g, 130.1 mmol) was dissolved in water (50 mL). Benzyl mercaptan (12.40 g, 100.0 mmol) was added dropwise and the solution stirred for 30 min. After adding carbon disulfide (7.60 g, 99.8 mmol) and one drop of Aliquat 336 the solution was stirred for another 30 min. The clear orange solution was cooled with ice water and thiophosgene (5.85 g, 50.9 mmol, 98%) added within 30 min. The solution turned dark red and a black, oily substance separated and solidified at the walls of the flask. Stirring was continued at room temperature for another 30 min. THF (75 mL) was added and the mixture stirred for another hour. The yellow solid was filtered off, washed with water and THF and dried at 50 °C. The product, **3a** was very slightly soluble

in organic solvents besides carbon disulfide and toluene. The yield was 12.90 g (58%) of yellow crystals, mp 161–162 °C (CS_2).

*4.3.3. Synthesis of **3a** and dibenzyl heptathiotricarbonate **2a** in diethylether.* Potassium benzyl carbonotrithioate **1a** (4.75 g, 19.9 mmol) was suspended in dry diethylether (30 mL) Thiophosgene (1.30 g, 11.3 mmol, 90%) in diethylether (20 mL) was added dropwise to an ice-cooled suspension thereof. The solution turned red. After 75 min the formed solid was filtered off, washed successively with diethylether, water and diethylether, and dried overnight at 50 °C to afford **3a** as a yellow powder. Yield: 2.25 g (51%), mp 160–161 °C (CS_2).

The organic solvent was evaporated and the remaining red oil (2.2 g) stored in the refrigerator overnight. The oil solidified and a further 0.55 g (12%) of **3a** was separated and washed with a few mL of THF. The residual oil was then purified by column chromatography on silica with pentane/ethylacetate (2:1), followed by another column separation with pure pentane as eluent. The isolated red oil/low melting solid, **2a** still contained a colorless impurity in all relevant fractions.

Yield: 0.35 g (8%).

^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ (ppm) 7.27–7.18 (10 H, m, Ar), 4.44 (4 H, s, CH_2).

^{13}C NMR (75.4 MHz, CS_2/$CDCl_3$): δ (ppm) 219.42 (C=S), 213.19 (C=S), 133.49, 129.21, 128.67, 127.90 (Ar), 43.32 (CH_2).

4.4. Reactions of 3a

*4.4.1. Reaction of **3a** with n-propylamine to dibenzyldisulfide **4** (aminolysis).* Compound **3a** (8.90 g, 10.1 mmol) was suspended in THF (100 mL) and *n*-propylamine (2.50 g, 42.3 mmol) added under stirring at room temperature. The stirring was continued for 60 min, whereupon **3a** dissolved and the solution turned orange-red. Precipitated sulfur was filtered off and the solvent removed. The residue was washed with water and the remaining crystals/oils extracted several times with pentane. After the removal of the solvent by evaporation a near colorless solid remained, which was recrystallized from pentane. The remainder from the extraction of **4** consisted of a multi-component orange oil. Colorless crystals, Yield: 3.85 g (78%), mp 70–71 °C (pentane) [mp lit.[9c] 71–72 °C].

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34–7.22 (10 H, m, Ar), 3.59 (4 H, s, CH_2).

^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 137.34, 129.39, 128.45, 127.40 (Ar), 43.26 (CH_2).

*4.4.2. Thermolysis of **3a** in chlorobenzene to bis(benzylsulfanyl thiocarbonyl)disulfide **5** and dibenzyl trithiocarbonate **6**.* Compound **3a** 4.45 g (5.0 mmol) was suspended in dry chlorobenzene (20 mL) and heated under reflux. The color of the solvent changed from yellow over green to dark red, while **3a** dissolved over time. After 2 h the reaction was stopped and the solvent removed. The dark red residue was extracted with pentane until the solvent stayed colorless. The remainder was partially soluble in diethylether and fully soluble in chloroform. It contained several yellow and red components, which were not further identified.

The pentane was again removed and the orange residue separated on silica by column chromatography with pentane as eluent. The fractions with the first two yellow components were collected and processed further.

The products were identified by their ^{1}H and ^{13}C NMR spectra, melting points and TLC comparison with independently prepared samples:

Bis(benzylsulfanyl thiocarbonyl)disulfide **5**, yellow crystals (0.20 g, 5%).

Dibenzyl trithiocarbonate **6**, yellow oil/crystals (0.30 g, 10%).

4.5. Synthesis of *O,O′*-diethyl pentathiotricarbonate 7

Potassium *O*-ethyldithiocarbonate **1c** (6.40 g, 39.9 mmol) was dissolved in dry benzene (30 mL). Thiophosgene (2.60 g, 22.6 mmol, ~90%) in benzene (10 mL) was added over 20 min under cooling with ice-water. The solution turned black and was stirred overnight. The solvent was removed by evaporation, the residue washed with water and the dark red oil extracted with pentane. After drying over sodium sulfate, the solvent was removed. The oil (5.40 g) was purified by column chromatography over silica with pentane as solvent.

Yield: 2.3 g (40%) of a dark red oil.

IR (neat) 1600, 1493, 1451, 1230, 1198, 1057, 756, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.68 (4 H, q, CH_3CH_2, J=6 Hz), 1.49 (6 H, t, CH_3CH_2, J=6 Hz).

^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 209.12 (C=S), 202.97 (C=S), 71.69 (CH_2), 13.39 (CH_3).

After two weeks storage at −5 °C parts of the oil crystallized. The separated solid was washed with diethylether until colorless and 1.3 g (22%) of the dimeric **8** was isolated.

4.6. Synthesis of *S,S′,S″,S‴*-1,3-dithietane-2,2,4,4-tetrayl-*O,O′,O″,O‴*-tetraethyl tetrakis(dithiocarbonate) 8[12]

Potassium *O*-ethyldithiocarbonate **1c** (8.00 g, 49.9 mmol) was suspended in dry diethylether (75 mL) at room temperature under stirring. Thiophosgene (2.60 g, 22.6 mmol, 90%) in dry diethylether (20 mL) was added dropwise over 20 min. The solvent turned red (not black as with benzene) and the solid slowly dissolved and a white precipitate separated out. After stirring for 75 min at room temperature, the solid **8** was filtered off, washed successively with water and diethylether. The solvent was evaporated and the red residue extracted with pentane. The resulting red oil (0.2 g, 3%) consisted mostly of *O,O′*-diethyl pentathiotricarbonate **7** and decomposed overnight at room temperature.

Yield: 5.45 g (95%) of a whitish powder, mp 163–164 °C (mp lit.[12] 161 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.54 (8 H, q, CH_3CH_2, J=7.2 Hz), 1.43 (12 H, t, CH_3CH_2, J=7.2 Hz).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ (ppm) 209.85 (C=S), 192.10 (CS_2), 69.12 (CH_2), 13.76 (CH_3).

The ^{13}C NMR signal for the quaternary carbon could not be unequivocally identified.

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14. Note: The X-ray analysis was performed on a Bruker Apex-II DUO CCD (Charge Coupled Device) Single Crystal X-ray Diffractometer, using graphite-monochromated MoKα radiation. Crystallographic data (excluding structure factors) for the structure **3a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary data No. CCDC 891881. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail deposit@ccdc.cam.ac.uk).