



Insertion of a two sulfur unit into the S–S bond—tailor-made polysulfides

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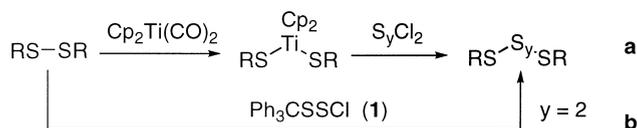
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Abstract

Triphenylthiosulfenyl chloride (**1**) reacts with disulfides RSSR, yielding tetrasulfides as the main products. The results of the insertion for different R groups are reported. A two-step mechanism involving the formation of unsymmetrical trisulfide intermediates containing the trityl group is proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Continuing interest in the area of organic polysulfides has resulted in new methods of synthesis of a variety of these naturally occurring compounds.¹ Once such a polysulfide is formed, it can be selectively desulfurized² but there is no easy method to allow the increase of a specific number of sulfur atoms. At present, the only available approach (applicable to cyclic polysulfides) involves first, insertion of dicarbonyl titanocene (difficult to handle) into the S–S bond,³ in turn, this is followed by nucleophilic substitution of the titanocene adduct by either SCl₂ or S₂Cl₂ sulfur chloride (S_yCl₂) as shown in Scheme 1a.



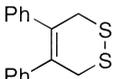
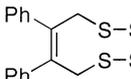
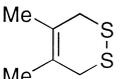
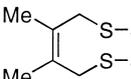
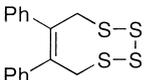
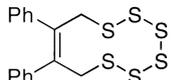
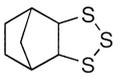
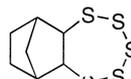
Scheme 1.

We report here a very convenient method to add two sulfur atoms to di- or higher sulfides (Scheme 1b). The transformation is carried out with triphenylmethylthiosulfenyl chloride (**1**).⁴ This compound is quite stable (for some years) when stored in the freezer. It has been used to transfer two sulfur atoms to 2,3-dimethylbutadiene but with limited success.^{5f} The best results

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were obtained with cyclic compounds containing S–S bonds (**12**, **14** and **17**) as well as with some primary alkyl disulfides **3** and **6** (Table 1). Lower selectivity and yields were observed for dibenzyl **8** and ditolyl **10** disulfides. Further addition of the 2-sulfur unit was usually slower and significantly less selective as in the conversion of **4** to **5**. The attempt to convert **15** to corresponding hexasulfide yielded a product that polymerized on isolation. In contrast, the hexasulfide **16** was quite stable and was obtained in 45% yield; it was easily crystallized. Its X-ray structure is presented in Fig. 1.⁶ Some cyclic polysulfides probably cannot be expanded by this method; norbornene pentasulfide **18** did not react even when using an excess of **1**.

Table 1

Substrate		Product	Ref. 5	Yield % ^a	
MeSMe	2	No reaction	-	-	-
MeS ₂ Me	3	MeS ₄ Me	4	a	81 (91)
MeS ₄ Me	4	MeS ₆ Me	5	a	b (71)
EtS ₂ Et	6	EtS ₄ Et	7	b	86 (89)
PhCH ₂ S ₂ CH ₂ Ph	8	PhCH ₂ S ₄ CH ₂ Ph	9	c	74 (74)
4-MeC ₆ H ₄ S ₂ C ₆ H ₄ Me-4	10	4-MeC ₆ H ₄ S ₄ C ₆ H ₄ Me-4	11	d	97 (80)
	12		13	e	87 (92)
	14		15	f	82 (85)
	13		16	g	47 (96)
	17		18	h	95 (100)

^a Tetrasulfides are not easily separable by column chromatography from other sulfides (usually starting material and some higher polysulfides); ^b Not isolated; the purity of products (NMR) is shown in brackets

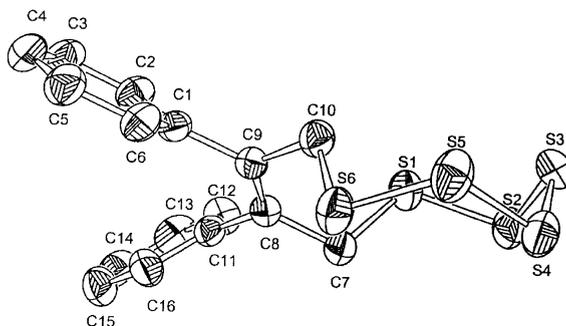


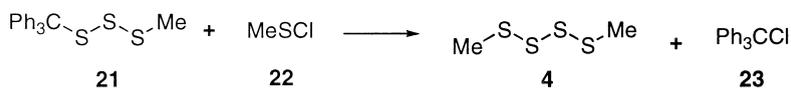
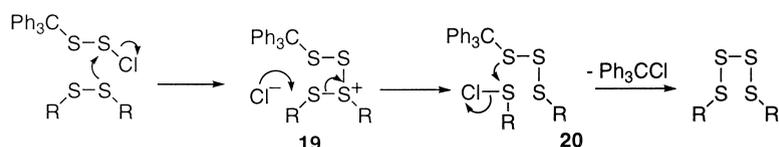
Figure 1. ORTEP drawing of C₁₆H₁₄S₆ (**16**). Selected bond distances (Å) and angles (degrees): S1–S2, 2.0371(9); S2–S3, 2.0514(9); S3–S4, 2.061(1); S1–C7, 1.838(2); C8–C9 1.344(2); C7–S1–S2, 103.52(7); S1–S2–S3 108.59(4); S2–S3–S4 107.03(3); S5–S4–S3 108.08(3); S6–S5–S4 108.67(4)

The reaction rate depended on the polarity of the solvent. The lowest rate was observed in hexane and the highest in acetic acid or acetic acid mixed with other solvents. Speeding up the reaction was important in the case of slowly-reacting compounds such as dibenzyl disulfide (**8**); a replacement of 1/3 of the methylene chloride with acetic acid resulted in a decreased reaction time from ca. 12 h to 30 min. The selectivity did not depend significantly on the solvent used. Nevertheless, it was found that the best results were obtained with solvents containing a significant proportion of acetic acid. An expected benefit from using highly polar trifluoroacetic acid did not materialize, resulting in a significant rate inhibition and excessive formation of higher polysulfides. The optimal reaction conditions appeared to involve a mixture of methylene dichloride and acetic acid in a 2:1 ratio. Using more acid did not result in any improvement. In turn, the use of smaller amounts of acetic acid decreased the reaction rate. Surprisingly, in the acetic acid/methylene chloride mixture, the selectivity of formation of tetrasulfide (ca. 90%) was not affected by the addition rate of the solution of reagent **1**. In the absence of acetic acid, yields were 10–15% lower.

We propose that thiosulfonyl chloride **1** was attacked by the sulfur of the disulfide to form a sulfonium salt **19**.⁷ The sulfonyl chloride (RSCl) that eventually formed and the trisulfide $\text{Ph}_3\text{C}\text{SSSR}$ (**20**) could equilibrate. The presence of the trityl leaving group attached to the terminal atom of sulfur of the trisulfide intermediate determines that this atom would react with the sulfonyl chloride. Even more importantly, the trityl group makes this reaction irreversible leading to a formation of tetrasulfide and trityl chloride (during separation by preparative chromatography, trityl chloride hydrolyzes and is isolated as trityl alcohol).⁸

The key argument in favour of the above mechanism was the isolation of the intermediate $\text{Ph}_3\text{C}\text{S}_3\text{Me}$ (**21**) from the reaction between dimethyl disulfide (**3**) and **1**. Compound **21** is crystalline⁹ and was isolated in 26% yield when the reaction was interrupted before the second step occurred. On treatment with separately prepared MeSCl (**22**)¹⁰ the intermediate formed tetrasulfide **4** in 72% yield (Scheme 2). Interestingly, although the isolated intermediate **21** was very pure, the tetrasulfide was contaminated with some tri- (2%), penta- (8%) and hexasulfide (8%). It is clear that there were other processes taking place; their origins are not clear at this time.

The scope of the reaction has certain limitations. For example, diisopropyl and di-*t*-butyl disulfides reacted eagerly with **1**, a mixture of products formed; none of them seemed to originate from the insertion. Probably, they are analogous to **20** ($\text{Ph}_3\text{CS}_x\text{R}$; $\text{R} = i\text{-Pr}, t\text{-Bu}, x = 3,4$) (Scheme 3).



In summary, this reaction allows an easy one-step conversion of disulfides to higher polysulfides. It should allow easy one-step access to some higher polysulfides unavailable by other methods.

Acknowledgements

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- The picture of **16** was printed from the cif file with Ortep-3 for Windows v. 1.06 created by: Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
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- A typical procedure: A solution of trityl thiosulfenyl chloride (**1**), 1 mmol (342 mg) in methylene chloride, was added rapidly into a solution of 1 mmol (122 mg) of diethyl disulfide (**6**) in a mixture of acetic acid and methylene chloride (disulfide was dissolved first in CH₂Cl₂; this is important when solid disulfides are used; slow-reacting disulfides were treated with 1.1 equiv. of **1**). The reaction time was usually shorter than 30 min except for **15** and **17** where at least 12 h was required for completion. The solvent was evaporated when the reaction mixture became colourless. Separation by column chromatography followed (the residue was loaded with minimum amount of benzene and eluted with hexanes). The product (160 mg) was analyzed by NMR revealing the presence of starting disulfide (2%) and hexasulfide (9%). The yield of Et₂S₄ was calculated as 75% based on starting disulfide.
- Properties of **21**: ¹H NMR (CDCl₃) δ = 2.3 (s, 3H), 7.35 (m, 15H); ¹³C NMR (CDCl₃) δ = 23.35, 73.15, 127.13, 127.84, 130.37, 143.48; m.p. 51–53°C; MS (EI) *m/z* 243 [M⁺-MeS₃] (100).
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