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SILICON IN ORGANOSULPHUR CHEMISTRY. Part 1. SYNTHESIS OF TRISULPHIDES

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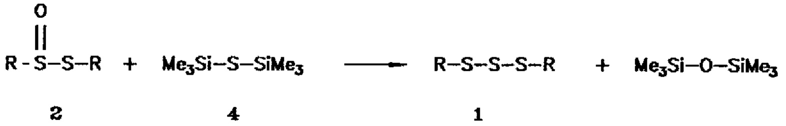
Summary. The reaction of bis(trimethylsilyl)sulphide with thiosulphinates and thiosulphonates in an inert solvent under neutral and mild conditions gives symmetrical alkyl- or aryl-trisulphides.

Little attention has been devoted to the synthesis of organic trisulphides, although this class of compounds seems highly promising from the reactional point of view. They have been prepared through a number of different methods, like the direct alkylation of alkali metal polysulphides,[1] the treatment of the "in situ" generated K_2S_3 under phase transfer conditions,[2] the reactions of mercaptans with sulphur containing electrophilic compounds,[1a,3] or the amine catalyzed reaction of mercaptans with elemental sulphur.[4]

We report in this communication a novel synthesis of symmetrical trisulphides **1**, through the reaction of thiosulphinates **2** or the thiosulphonate **3** with bis(trimethylsilyl)sulphide **4**. Few reports on the reactivity of silylated sulphides with compounds containing an $S=O$ functionality have appeared in the literature.[5]

When the silylsulphide **4** is reacted with the thiosulphinates **2** in anhydrous chloroform at 60° C, the trisulphides **1** and hexamethyldisiloxane are formed (Equation 1). The latter is removed together with the solvent by vacuum distillation leaving almost pure **1**.

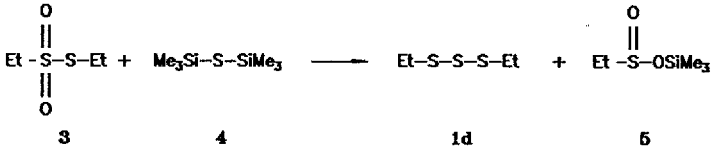
Similarly S-ethyl ethylthiosulphonate **3**, as representative example of this class of compounds, is reacted with **4**, under the same reaction conditions, to give the trisulphide **1d** together with the silyl esters **5** (Equation 2).



$$R\text{-}\overset{\overset{O}{\|}}{S}\text{-}S\text{-}R + Me_3Si\text{-}S\text{-}SiMe_3 \longrightarrow R\text{-}S\text{-}S\text{-}S\text{-}R + Me_3Si\text{-}O\text{-}SiMe_3 \qquad (1)$$

$$\mathbf{2} \qquad \mathbf{4} \qquad \mathbf{1}$$

R = Me, Ph, p–Tol



$$Et\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}S\text{-}Et + Me_3Si\text{-}S\text{-}SiMe_3 \longrightarrow Et\text{-}S\text{-}S\text{-}S\text{-}Et + Et\text{-}\overset{\overset{O}{\|}}{S}\text{-}OSiMe_3 \qquad (2)$$

$$\mathbf{3} \qquad \mathbf{4} \qquad \mathbf{1d} \qquad \mathbf{5}$$

Both reactions proceed essentially under neutral conditions thus avoiding any rearrangement of the trisulphides obtained. All compounds were identified by NMR, GC-MS and comparison of the literature reported physical properties. Yields are generally high, and no traces of the corresponding higher order polysulphides has ever been detected in the reaction mixture.[6]

Examples of this reactivity are reported in the Table.

Table. Reactions of thiosulphinates 2 and thiosulphonate 3 with bis(trimethylsilyl)sulphide 4. [a]

Reagent	Time (h)	Product (yields %)	m.p.(b.p.,mmHg) °C	Lit. m.p.(b.p.,mmHg) °C
MeS(O)SMe 2a	14	MeSSSMe (73) 1a	65–68,25 mmHg	58–59,15 [7]
PhS(O)SPh 2b	16	PhSSSPh (95) 1b	oil	oil [3g]
p–TolS(O)STol–p 2c	16	p–TolSSSTol–p (90) 1c	79–80	82–84 [3e]
$EtSO_2SEt$ 3	12	EtSSSEt (95) 1d	81–83,3 mmHg	92–97,26 [8]
		$EtS(O)OSiMe_3$ (–) [b] 5	–	–

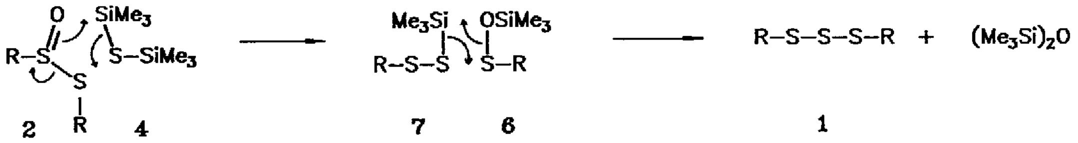
[a] In $CHCl_3$ at 60 °C

[b] Recognized by GC–MS and NMR, it was hydrolized before purification of 1d

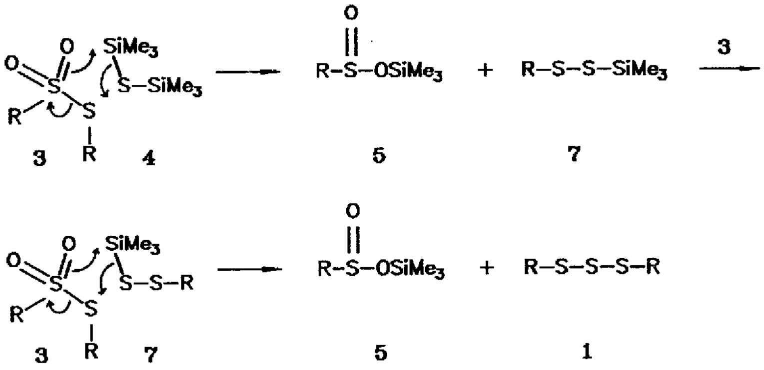
Due to the easier synthesis and handling of the thiosulphonates with respect to the thiosulphinates, the method for the synthesis of trisulphides described in Equation 2 seems more convenient than that reported in Equation 1.

The first step of the reactions might be the silylation at the oxygen by the silylsulphide 4 to give ionic intermediates that evolve to the products; however it seems more appropriate to draw for the two reactions the concerted mechanisms outlined in Schemes 1 and 2.

Scheme 1



Scheme 2



The formation of silyl sulphenate ester 6 and the silylated disulfide 7 is suggested in Scheme 1. Silyl esters of only a few aryl sulphenic acids are known.[9] Their reactivity suggests highly electrophilic sulphur atom, which can react with the silylated disulphide 7 to give the observed products.

The intermediacy of the silylated disulphides 7 is also proposed for the reaction of the thiosulphonates 3 with 4 (Scheme 2). Indeed, in the case of the reaction of $EtSO_2SEt$ 3 with 4, carried out using a tenfold excess of 4, we were able to detect by GC-MS the ethyl(trimethylsilyl)disulphide intermediate 7 (R = Et).[10]

Interesting feature of this new preparations appears the very mild and above all neutral reaction conditions. Starting materials are commercial or available through well established synthetic procedure.

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References and notes

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6. The preparation of dimethyltrisulphide **1a** may be representative of a typical experimental procedure. S-Methyl methylthiosulphinate **2a** (1g, 9 mmol.) is dissolved in anhydrous chloroform and treated with 1.62 g (9 mmol) of bis(trimethylsilyl)sulphide. The reaction mixture is heated to 60° C with stirring for 14 h, diluted with methylene chloride and washed several times with water. The crude material obtained is distilled under vacuum to obtain 830 mg of pure material (72.8 % yield).

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10. The yield of $EtSSSiMe_3$ was calculated about 80%, assuming for the silylated disulphide a GC response factor similar to that of the diethyltrisulphide **1d**.

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