

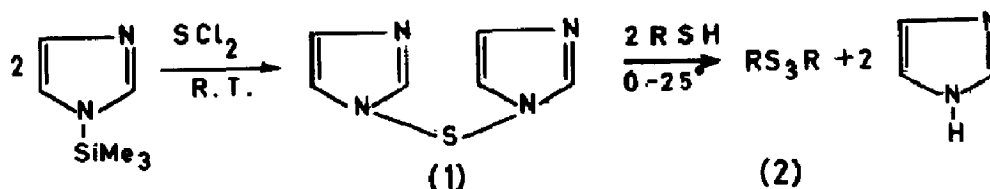
A NEW SYNTHESIS OF ORGANIC TRISULFIDES

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Abstract: Thiols react with diimidazolylsulfide under mild conditions to give symmetrical trisulfides in good yield and high purity.

During screening of natural products for insecticidal activity we found that allyl di- and trisulfides show considerable larvicidal activity.¹ It was, therefore, of interest to synthesise different di- and trisulfides and to test their bioactivities. Though several excellent methods for the synthesis of disulfides are described, only few are available for trisulfides.² This is mainly because of the greater thermal instability of trisulfides.³ In this communication a new one-pot synthesis of symmetrical trisulfides is described. The reaction takes place at low temperatures (0-25°) and trisulfides are obtained in high purity and excellent yield.



The synthesis is based on the high reactivity of diimidazolylsulfide towards nucleophiles. Diimidazolylsulfide (1) is readily obtained⁴ by the reaction of N-trimethylsilylimidazole with sulfur dichloride. A solution of thiol (2 molar equivalents) in hexane is added to the stirred suspension of (1) at 0 to 25°. Almost instantaneous reaction takes place with the precipitation of imidazole. After stirring for 30 min. imidazole is filtered off. Trace amounts of imidazole present in the hexane filtrate are removed by washing with water. The trisulfides (2) may be further purified by column chromatography (SiO₂). The products obtained after chromatography contain more than 98% of the desired trisulfides in excellent yield. The trisulfides were characterised by GC-MS, NMR, HPLC and GLC and comparison with known compounds. Representative examples of the synthesis are shown in the table.

A typical example of the synthesis is given below :

Sulfur dichloride (1.45 gm, 0.014 mol, freshly distilled) in hexane was added under dry conditions, to a stirred hexane solution of N-trimethylsilylimidazole (4 gm, 0.028 mol) at room temperature. A finely divided precipitate of diimidazolylsulfide was obtained. After stirring for 30 min., the mixture was cooled to 0° and a solution of freshly distilled allyl thiol (2.11 gm 0.028 mol) in dry hexane (10 ml) was added dropwise (20 min.). Immediate reaction takes place. After stirring for another 30 min., the precipitated imidazole was removed by filtration. The filtrate was washed with water and dried (Na₂SO₄) and the solvent was removed under vacuum. The residue which analysed for 98% allyl trisulfide by GLC, was purified by column chromatography (SiO₂ pentane as eluant), Yield 2.02 gm (80%); b. p. 92°/6.0 mm.

T A B L E

(2) R	Reaction conditions (Time, temp.)	Yield ^a (%)	b. p. /m. p.	Lit. b. p. /m. p.	Mol. Formula Mass spectra m/e (M ⁺)
Allyl	30 min; 0°	80	92°/6mm	-	C ₆ H ₁₀ S ₃ (178)
<i>n</i> -Propyl	30 min; 25°	80	58°/0.5mm	65°/0.5mm ⁽⁵⁾	C ₆ H ₁₄ S ₃ (182)
<i>iso</i> -Propyl	30 min; 25°	80	51°/0.15mm	56°/2mm ⁽⁵⁾	C ₆ H ₁₄ S ₃ (182)
<i>n</i> -Butyl	30 min; 25°	90	103°/4mm	137-40°/12mm ⁽⁶⁾	C ₈ H ₁₈ S ₃ (210)
<i>t</i> -Butyl	30 min; 25°	90	78°/3mm	75-78°/3mm ⁽⁵⁾	C ₈ H ₁₈ S ₃ (210)
<i>n</i> -Amyl	30 min; 25°	86	150°/4mm	-	C ₁₀ H ₂₂ S ₃ (238)
Benzyl	2 h, 0°	66	49°	49-50° ⁽⁵⁾	C ₁₄ H ₁₄ S ₃ (278)
Phenyl	2 h, 0°	80	Oil	Oil ⁽⁵⁾	C ₁₂ H ₁₀ S ₃ (258)

a) Yields are not optimised, Yields refer to isolated products(SiO₂ chromatography) containing >98% trisulfides (GLC and/or HPLC)

b) Mass spectra of the pure compounds were recorded by GC-MS (Micromass 7070F). Expected ratio of intensities of M⁺ and M⁺+2 were obtained for molecular formulae.

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