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SYNTHESIS OF CYCLIC TRISULFIDES BY USING SILYL AND TIN SULFIDES

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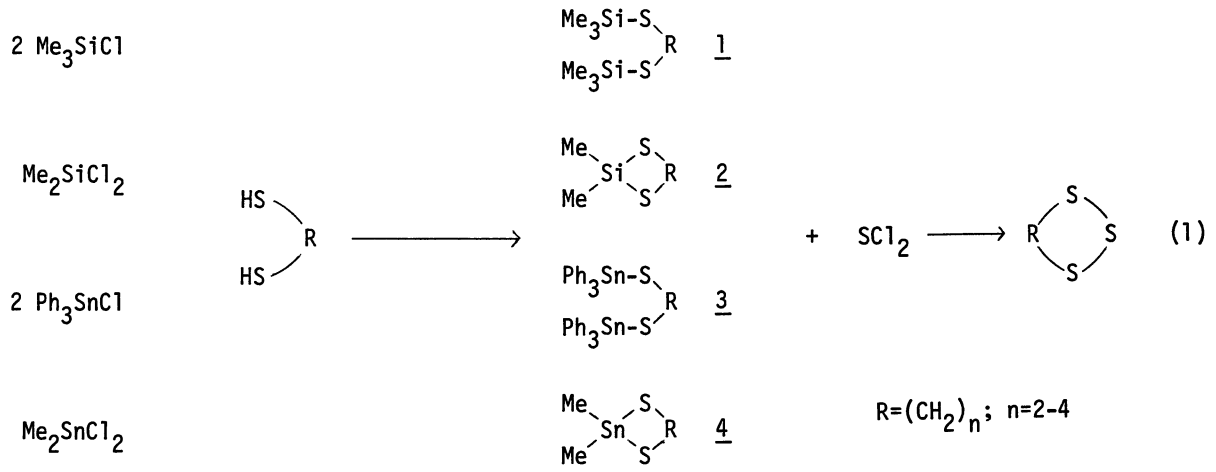
Sulfur dichloride was allowed to react with linear and cyclic, silyl and tin sulfides prepared from alkanedithiols. Of the sulfides, bis(trimethylsilyl) sulfides were most effective for synthesis of cyclic trisulfides.

Though a variety of organic trisulfides have been known, their cyclic derivatives are less common. Of natural products bicyclic trisulfides Sporidesmin E is found in the fungus Pitomyces chartarum[1] and two other cyclic trisulfides have been reported.[2,3] Few useful synthetic method, however, has yet been developed for these compounds.[4] Now we wish to report a useful synthetic approach for cyclic trisulfides using silyl and tin sulfides.

In order to synthesize cyclic trisulfides we tried to use silyl and tin sulfides which have been employed to obtain linear trisulfides.[5,6] It was found



that bis(trimethylsilyl) sulfides were most effective for synthesis of cyclic trisulfides among a variety of silyl and tin sulfides. As shown in Scheme 1, silyl and tin sulfides with linear and cyclic structures were prepared from alkanedithiols,[7,8,9] and were allowed to react with sulfur dichloride to obtain cyclic trisulfides.

First, a series of silyl and tin sulfides (1-4) was prepared by reaction of dithiols with appropriate silyl and tin chlorides in the presence of triethylamine and by successive distillation or recrystallization (Table 1). These sulfides were obtained in fairly good yields, except the reaction of butanedithiol with dimethyldichlorosilane which gave oligomers.

Table 1. Preparation of silyl and tin sulfides(1-4)[a]

Si and Sn sulfide \ -R-	Yield,% (lit.) $-(CH_2)_2-$	$-(CH_2)_3-$	$-(CH_2)_4-$
1	76(7)	55(7)	78[b]
2	60(8)	26(9)	0[c]
3	–	76[d]	70[e]
4	51(8)	56(9)	56[f]

[a]Reaction conditions were according to the procedure by Wieber et al.[9] [b]Bp 81-83°C(0.2 mmHg); ^{1}H NMR(CCl_4): 2.43(t,4,J=6Hz, SCH_2), 1.67(m,4,CH_2), 0.28(s,9,$SiCH_3$). [c]Oligomerization occurred. [d]Recrystallized from hexane/benzene=2/1(v/v), mp 120-122°C; ^{1}H NMR($CDCl_3$): 8.2-6.8(m,30,SnC_6H_5), 2.55(t,4,J=7Hz, SCH_2), 1.68(m,2,CH_2). [e]Recrystallized from hexane/benzene= 1/1(v/v), mp 124-127°C; ^{1}H NMR($CDCl_3$): 7.7-6.8(m,30,SnC_6H_5), 2.36(t,4,J=6Hz,SCH_2), 1.48(m,4,CH_2). [f]Bp 125°C(0.05 mmHg); ^{1}H NMR($CDCl_3$): 2.70(m,4,SCH_2), 1.73(m,4,CH_2), 0.70(s,6,$SnCH_3$).

Next, synthesis of cyclic trisulfides was carried out by treatment of the resulting silyl and tin sulfides with sulfur dichloride in THF. A typical procedure is as follows: to 1,3-propanedithiobis(trimethylsilane) (433 mg, 1,72 mmol) in THF (90 ml) cooling with ice bath was added dropwise sulfur dichloride (180 mg, 1.80 mmol) in THF (10 ml) under nitrogen atmosphere, and the reaction mixture was stirred for 24 hr at room temperature. After solvent and trimethyl-

chlorosilane were evaporated under reduced pressure, the residue was separated by preparative TLC (hexane as developing solvent) to give 1,2,3-trithiane (178mg,75%).

The results are shown in Table 2. None of the silyl and tin sulfides from ethanedithiol provided cyclic trisulfide, 1,2,3-trithiolane because of its ring strain, and only its oligomers were detected by HLC. On the other hand, the reaction of those from propanedithiol with sulfur dichloride in THF (1.8×10^{-2}mol/l) for 24 hr at room temperature resulted in the formation of cyclic trisulfide, 1,2,3-trithiane in good yield, which was isolated by preparative TLC and identified by ^{1}H NMR, MS, IR, and melting point.[10] Of these four silyl and tin sulfides, linear silyl sulfide, 1,3-propanedithiobis(trimethylsilane) gave the product in the highest yield (75 %). The yield decreased to 31% when higher concentration (1.2×10^{-1}mol/l) of the silyl sulfide was used. Similarly seven membered ring trisulfide, 1,2,3-trithiepane[11] was isolated in 66% yield.

Directly 1,3-propanedithiol instead of the bis(trimethylsilyl) sulfide was allowed to react with sulfur dichloride in the presence of triethylamine under similar conditions affording the cyclic trisulfide only in 43% yield.

Table 2. Synthesis of cyclic trisulfides

Si and Sn sulfide \ Cyclic trisulfide			
	Yield(%)		
1	oligomers	75(31)[a] (43)[b]	66
2	oligomers	49	—
3	—	36	9
4	oligomers	30	8

[a]The concentration of the solution was 1.2×10^{-1}mol/l.
[b]Instead of the silyl sulfide 1,3-propanedithiol was used together with Et_3N.

These results indicate that the preparation of cyclic trisulfides through trimethylsilylation of dithiols possesses advantages over conventional method.[4,10,11] Starting materials, bis(trimethylsilyl) compounds, are easily prepared from dithiols in high yields and trimethylchlorosilane produced in the subsequent

reaction is simply removed by evaporation in vacuo. The cyclic trisulfides obtained are isolated in high yields by preparative TLC.

Extension of this cyclization process to synthesis of various cyclic polysulfides is now under investigation.

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