

## A New Route to 1,2,3-Propanetrithiol

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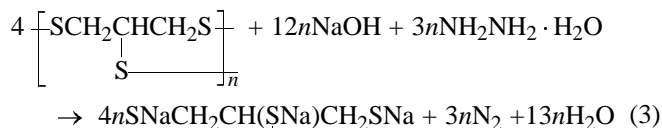
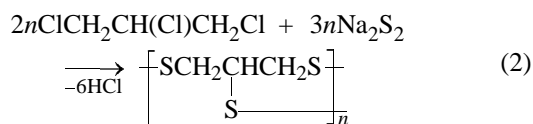
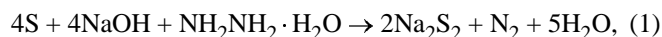
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**Abstract**—A new procedure was developed for preparing 1,2,3-propanetrithiol from available initial compounds. 1,2,3-Trichloroethane reacts with sodium disulfide prepared by dissolving sulfur in the system NaOH–N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O–H<sub>2</sub>O to give a disulfide dendrimeric polymer, thiokol, in almost quantitative yield. This polymer is subjected to reductive cleavage with an alkaline solution of hydrazine hydrate, which is followed by acidification with HCl. The yield of 1,2,3-propanetrithiol exceeds 60%. The synthesis can be performed as a one-pot procedure.

1,2,3-Propanetrithiol CH<sub>2</sub>(SH)CH(SH)CH<sub>2</sub>(SH) can be used as complexing agent, antidote against heavy metals, curing agent for epoxy resins, monomer for preparing high-sulfur polymers, etc.

The known routes to 1,2,3-propanetrithiol are based on the reaction of 1,2,3-tribromopropane with sodium hydrosulfide [1, 2]. The target product is isolated by extraction and precipitation in the form of lead mercaptide, from which it is recovered by acidification. Then it is steam-distilled, extracted with ether, and only after these procedures isolated by distillation. A procedure for preparing 1,2,3-propanetrithiol by reaction of trihalopropanes with sodium hydrosulfide in the presence of DMSO, DMF, or their mixtures with alcohol was proposed in [3]. The target product was obtained only as a mixture with the initial trihalopropanes.

We have performed a reaction of 1,2,3-trichloropropane with a solution of sulfur in the system hydrazine hydrate–alkali–water [4] and obtained a strongly cross-linked disulfide dendrimeric polymer, thiokol. Reductive cleavage of the resulting polymer with an alkaline solution of hydrazine hydrate, followed by acidification with hydrochloric acid, yields 1,2,3-propanetrithiol:



The influence of reaction conditions on the yield of 1,2,3-propanetrithiol is illustrated by the table. Optimization of the conditions for synthesis and reduction of the dendrimer (thiokol) allowed the yield of 1,2,3-propanetrithiol to be increased to 61%. The best conditions are as follows. Sulfur is dissolved in an aqueous alkali solution in the presence of hydrazine hydrate at 80–90°C. Sulfur should be taken in a slight excess relative to alkali, in order to minimize the formation of Na<sub>2</sub>S (or K<sub>2</sub>S). The optimal range of the NaOH to S molar ratios is from 1 : 1.1 to 1 : 1.5. Hydrazine hydrate is taken in a 4–5-fold excess relative to the stoichiometry. This excess favors faster dissolution of sulfur and more selective formation of S<sub>2</sub><sup>2-</sup> ions in solution.

The solution of sulfur (actually of sodium disulfide) is alkylated at 40–50°C with 1,2,3-trichloropropane taken in approximately stoichiometric amount relative to the alkali taken for sulfur dissolution. A significant excess of alkali (and hence of the sulfur solution) is not appropriate, because it results in excessive consumption of chemicals and complicates isolation of the target product. After adding the calculated amount of 1,2,3-trichloropropane, the reaction mixture is heated to 80–90°C for 1 h to bring the reaction to completion. The precipitated white powdery dendrimer, after cooling to 20–25°C, is filtered off, washed with water, and dried. Yield >90%. The reductive cleavage of the dendrimer is performed with an alkaline solution of hydrazine hydrate at 80–90°C. In this case alkali is taken in a slight excess relative to the stoichiometry (molar ratio from 1 : 3.5 to 1 : 4). The reaction mixture is cooled and acidified with HCl to pH ~6. 1,2,3-Propanetrithiol is extracted with an organic solvent (ether or methylene chloride). Synthesis can be performed as a one-pot procedure after washing the dendrimer by decanting or with a siphon; its drying is not necessary.

Synthesis conditions and yield of 1,2,3-propanetrithiol<sup>a</sup>

Reactants taken, g (mol)			Reaction time, h	Yield of 1,2,3-propanetrithiol	
dendrimer	NaOH	N <sub>2</sub> H <sub>4</sub> · H <sub>2</sub> O		g	% based on dendrimer
2.5 (0.018)	3.3 (0.08)	15 (0.3) <sup>b</sup>	1.0	1.2	48
3.3 (0.024)	4.3 (0.1)	20 (0.4) <sup>b</sup>	1.0	1.1	32
4.0 (0.029)	4.9 (0.122)	24 (0.48) <sup>c</sup>	1.0	2.2	53
9.0 (0.066)	11.4 (0.285)	54 (1.08) <sup>c</sup>	1.5	5.0	54
9.0 (0.066)	11.4 (0.285)	54 (1.08) <sup>c</sup>	1.0	4.7	46
9.0 (0.066)	11.4 (0.285)	54 (1.08) <sup>d</sup>	1.5	5.4	58
13.0 (0.095)	17.0 (0.425)	78 (1.56) <sup>d</sup>	1.0	7.8	59
9.0 (0.066)	11.4 (0.285)	54 (1.08) <sup>d</sup>	2.5	3.7	40
4.0 (0.029)	4.9 (0.122)	24 (0.48) <sup>d</sup>	1.0	2.5	61
4.0 (0.029)	4.9 (0.122)	24 (0.48) <sup>d</sup>	0.5	1.2	29

<sup>a</sup> The dendrimer is reduced at 85–90°C; extraction is performed with dichloromethane. <sup>b</sup> The mixture was acidified to pH 1.

<sup>c</sup> The mixture was acidified to pH 6. <sup>d</sup> The mixture was acidified to pH 7.

Our procedure utilizes commercially available chemicals: trichloropropane, sulfur, alkali (NaOH or KOH), and hydrazine hydrate. The resulting product is relatively pure (~95%); it is readily isolated from the reaction mixture and can be used in syntheses without distillation.

### EXPERIMENTAL

The NMR spectra were taken on a Bruker DPX-400 spectrometer (400 MHz, CDCl<sub>3</sub>, internal reference HMDS).

**Synthesis of the dendrimer.** A four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and an attachment for loading reactants was charged with 4 g of NaOH, 30 ml of water, and 5 ml of hydrazine hydrate. The mixture was stirred until the alkali completely dissolved, and 4.16 g of powdered sulfur was added. The resulting mixture was stirred for 1 h at 80–90°C and cooled to 45°C, after which 4.86 g of 1,2,3-trichloropropane was added at the temperature maintained within 40–50°C. Then the mixture was heated for 1 h at 80–90°C. After cooling, the precipitate was filtered off, washed with water, and dried. Yield of cross-linked thiokol 4.5 g (95%). Because the yield of the dendrimer is almost quantitative, it can be washed in the same flask by decanting, with the subsequent reductive cleavage being performed in the same vessel by adding the calculated amount of the redox system.

**Reduction of thiokol** (see also table). A four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and an attachment for loading reactants was charged with a solution of 4.62 g of NaOH in 30 ml of hydrazine hydrate, and 4 g of thio-

kol was added. The mixture was heated to 80–90°C for 1 h. After cooling, the mixture was carefully acidified with HCl to pH ~6. An oily liquid separated, which was extracted with ether or methylene chloride. The extract was dried over CaCl<sub>2</sub>. After removing the solvent, 95% pure (GLC data) 1,2,3-propanetrithiol was obtained. Yield 2.72 g (59%); bp 102–105°C (7 mm Hg) [1], 95°C (1 mm Hg) [2]. The IR spectrum contains a strong band at 2540 cm<sup>-1</sup>, corresponding to the SH stretching vibrations, and also bands belonging to CH<sub>2</sub> and CH vibrations.

In the <sup>1</sup>H NMR spectrum, the protons of the terminal SH groups give rise to a triplet at 1.63 ppm (*J* 8.5 Hz), and the proton of the central SH group, to a doublet at 1.95 ppm (*J* 8.0 Hz). The CH<sub>2</sub> and CH protons give a complex multiplet centered at 2.96 ppm. The intensity ratio of the above-given signals is 2 : 1 : 5.

### ACKNOWLEDGMENTS

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