

Short Communications

1,3-Dimercaptoacetone and Some Derivatives

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In 1924 Groth¹ prepared phenacylmercaptan and two years later the first aliphatic α -ketomercaptan, namely acetonylmercaptan². Hromatka and Engel³ as late as 1948 independently investigated the same substance with some differing results, which will be discussed in another communication.

No substance known to the author, however, is described in the literature which contains two mercapto groups in α -position to the keto group. Now experiments to prepare 1,3-dimercaptoacetone have been carried out.

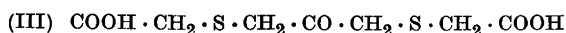
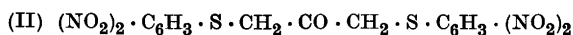
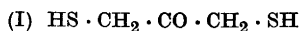
Groth² treated monochloro-acetone with dithiocarboxy-glycolic acid (prepared from carbon disulfide and glycolic acid in an alkaline medium) and from the product he obtained acetonylmercaptan in good yield. When the analogous reaction was performed with 1,3-dichloroacetone, however, some derivatives of 1,3-dimercaptoacetone (I) could be obtained, but every attempt to prepare the mercaptan from these failed. Experiments with potassium xantogenate and "Benders salt", $C_2H_5O \cdot CO \cdot SK$, led

to similar results. The derivatives, obtained in these reactions, will be discussed in a later communication.

Analogously to the reaction, described by Hromatka and Engel³, sodium sulfhydrate was treated with 1,3-dichloroacetone, and thus 1,3-dimercaptoacetone could be prepared in about a 64 % yield. The substance is soluble in ordinary organic solvents in the hot but it is rather difficult to recover it from the solutions.

1,3-Bis-(2,4-dinitrophenyl-mercapto)-acetone (II) and 1,3-bis-(carboxy-methylmercapto)-acetone (III) could be prepared from the mercaptan by reaction with 2,4-dinitro-chloro-benzene and monobromoacetic acid resp. The dicarboxylic acid (III) could also be obtained from 1,3-dichloroacetone and thioglycolic acid. The two substances behaved in a similar manner, and the mixture showed no melting-point depression. In some of these reactions pyridine has been used as a solvent with advantage.

The equivalent weight was determined by titration with an 0.1 N iodine solution, each mercapto group corresponding to one atom of iodine. A qualitative test to the mercapto group could be obtained by Rheinboldt's reaction⁴. Characteristic precipitates were obtained with *e. g.* lead acetate and zink sulfate in alcoholic solutions of 1,3-dimercaptoacetone. Experiments with the mercaptan indicate that the



substance may be dimeric. Investigations are being pursued.

Experimental. *1,3-Dimercaptoacetone.* A solution of 4.0 g (0.10 mole) of sodium hydroxide in 40 ml of water was saturated with hydrogen sulfide and cooled to about 5° by means of an ice bath, 6.4 g (0.05 moles) of 1,3-dichloroacetone, dissolved in 30 ml of alcohol, being introduced dropwise with stirring, while the temperature was kept low. The dimercaptan precipitated during the addition and was separated by filtration with suction, and then washed with about 200 ml of water. The product was dried in a vacuum desiccator over concentrated sulfuric acid. Melting point 85–86°. Yield 3.9 g (64 %).

$C_3H_6OS_2$ (122.17)	C	H	S
Calc.	29.47	4.95	52.48
Found	29.71	4.74	52.50

Equiv. wt. Calc. 61.1 Found 63.0; 62.9

1,3-Bis-(2,4-dinitrophenyl-mercapto)-acetone. According to the general process 5 1.22 g (0.01 mole) of 1,3-dimercaptoacetone was treated with 4.06 g (0.02 moles) of 2,4-dinitro-chloro-benzene. However, pyridine was used with advantage as a solvent instead of sodium hydroxide solution. A yellow product precipitated, was filtered and washed with some water and acetone. The crude product was recrystallized from acetone and was finally obtained as small, yellow, glistening crystals. Melting point 198–200°. Yield 3.5 g (78 %).

$C_{15}H_{10}O_9N_4S_2$ (454.23)	Calc.	N	12.33
	Found »	12.21	

1,3-Bis-(carboxy-methyl-mercapto)-acetone. A. A solution of 13.9 g (0.10 mole) of monobromo-acetic acid in 25 ml of water was neutralized with 4.0 g (0.10 mole) of sodium hydroxide, dissolved in

10 ml of water and added drop by drop with cooling and vigorous stirring to 6.1 g (0.05 moles) of 1,3-dimercaptoacetone, dissolved in a solution of 4.0 g (0.10 mole) of sodium hydroxide in 30 ml of water. The stirring was continued for half an hour. The solution was then diluted with water and dropped into a mixture of concentrated hydrochloric acid and ice. The dicarboxylic acid precipitated as small crystals, was filtered and washed with some water. The acid could be recrystallized from water or ligroin (b. p. 60–70°). Melting point 148–150°. Yield 7.9 g (66.5 %).

Equiv. wt. Calc. 119.1 Found 119.7

B. 9.2 g (0.10 mole) of thioglycolic acid, dissolved in 25 ml of alcohol, was neutralized with a solution of 11.2 g (0.20 moles) of potassium hydroxide in 60 ml of diluted alcohol (1 : 1). The dipotassium salt separated as an oil; 6.4 g (0.05 moles) of 1,3-dichloroacetone, dissolved in 35 ml of alcohol, was added dropwise with cooling and stirring, and after a while the oily phase disappeared. After some hours the solution was dropped into hydrochloric acid and ice, and the acid was separated as in A. Melting point 148–150°. Yield 7.1 g (59 %).

$C_7H_{10}O_5S_2$ (238.20)	Equiv. wt.	C	H	S
Calc.	119.1	35.26	4.23	26.91
Found	120.0	35.38	4.10	26.73

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