

bine with hydrogen bromide as readily as do ethylenic ketones, and the mode of addition is the same in both cases.

2. Ammonia transforms these substances into stereo-isomers which do not combine with hydrogen bromide

3. Although these cyclopropane derivatives are constituted like secondary nitro compounds they do not form metallic derivatives.

4. Concentrated alkalis remove nitrous acid from the nitrocyclopropanes and transform them into diketones. The probable steps in this process are: first, elimination of nitrous acid; second, rearrangement of the resulting cyclopropane to an acetylenic ketone; third, addition of water to the ketone.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## SESQUI-MUSTARD GAS OR BIS- $\beta$ -CHLORO-ETHYL ETHER OF ETHYLENE DITHIO-GLYCOL

BY RAPHAEL ROSEN AND E. EMMET REID

Received December 2, 1921

In view of the remarkable properties shown by  $\beta\beta'$ -dichloro-ethyl sulfide, it seemed of interest to prepare a compound of the same type but having 2 sulfur atoms separated by an ethylene group,  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{-CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ , with a view to comparing the chemical and physiological properties with those of the monosulfur compound.

Two ways of preparing the corresponding dihydroxy compound were studied; (1) the reaction of the sodium salt of monothio-glycol on ethylene bromide and (2) of ethylene chlorohydrin on the sodium salt of ethylene dithio-glycol.

**Preparation of Monothio-ethylene Glycol,  $\text{HSCH}_2\text{CH}_2\text{OH}$ .**—Our work with this compound was done before the paper of Bennett<sup>1</sup> came to hand, but our conclusions agree well with his, though our yields were not so good. We, too, had great difficulty in repeating the work of Carius.<sup>2</sup> In a number of experiments, in which his directions were followed as closely as possible, we obtained only insignificant yields.

The best method we found to be as follows.

Two hundred and forty g. of crystallized sodium sulfide is melted on the water-bath and saturated with hydrogen sulfide; 150 g. of alcohol is added and the mixture resaturated. To this solution, which is kept below 20°, 120 g. ethylene chlorohydrin is added slowly. This material is allowed to stand for 36 hours at room temperature. Then hydrogen chloride is passed in until the mixture is acid, and the sodium chloride filtered off. The filtrate is fractionated under reduced pressure. The yield was 26 to

<sup>1</sup> Bennett, *J. Chem. Soc.*, **120**, 422 (1921).

<sup>2</sup> Carius, *Ann.*, **124**, 257 (1862).

30% of the pure mercaptan boiling at 52° at 12 mm. The mercaptan is colorless, has a characteristic odor and is very soluble in water, in alcohol and in ether.

The residue from the distillation, after the removal of sodium chloride, is a sirupy liquid containing ethylene disulfide which is precipitated by the addition of water, and  $\beta\beta'$ -hydroxy-ethyl sulfide which was identified by being transformed into mustard gas by conc. hydrochloric acid.

The lead compound of the mercaptan is yellow and only slightly soluble in alcohol. The mercurous compound is a white crystalline solid, soluble in hot alcohol and melting at 108°.

In alkaline solution, it reacts like other mercaptans;<sup>3</sup> a sulfonic acid group in the  $\alpha$  position in anthraquinone is replaced to give compounds of the type  $C_{14}H_7O_2.SCH_2CH_2OH$ . A number of these have been made in this Laboratory and will be reported later.<sup>4</sup>

Dithio-ethylene glycol was prepared by the method of Fasbender<sup>5</sup> as modified by Hoffman and Reid<sup>4</sup> in this Laboratory. The original method yields a product containing 74% of the mercaptan, but, by distilling the reaction mixture in a vacuum instead of with steam, the pure mercaptan is obtained. This mercaptan can be determined by the method of Kimball, Kramer and Reid,<sup>6</sup> provided the mixture stands overnight after the addition of the iodine and before titration.

**Bis- $\beta$ -hydroxy-ethyl Ether of Ethylene Dithio-glycol.**— $HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$ .—To a mixture of 15 g. of monothio-ethylene glycol and 18 g. of ethylene bromide, 8 g. of powdered sodium hydroxide was added in small portions and the mixture was refluxed for an hour. The reaction product was extracted repeatedly with boiling ether. A flaky white substance separated as the extract cooled. This was recrystallized from absolute alcohol. The compound is waxy and hygroscopic and melts at 114–711°. On account of its properties it is difficult to purify, which explains the high sulfur content found, *viz.*, 37.39% instead of the calculated value, 35.18%.

The same compound was obtained from dithio-ethylene glycol and ethylene chlorohydrin in a similar way.

Attempts to prepare this compound by the use of alcoholic potash instead of the powdered sodium hydroxide were fruitless; a white flaky substance, insoluble in all common solvents and unreactive with the usual reagents, was always obtained. It is probable that vinyl derivatives are formed at first and that these polymerize to give the insoluble substance.<sup>7</sup>

<sup>3</sup> Reid, Mackall and Miller, *THIS JOURNAL*, **43**, 2104 (1921).

<sup>4</sup> Hoffman and Reid, unpublished work.

<sup>5</sup> Fasbender, *Ber.*, **20**, 460 (1887).

<sup>6</sup> Kimball, Kramer and Reid, *THIS JOURNAL*, **43**, 1199 (1921).

<sup>7</sup> After this article had been submitted, that of Bennett and Whincop (*J. Chem. Soc.*, **120**, 1860 (1921)) came to hand. They prepared the same compound in alcohol solution and speak of a "quantitative yield." I have asked Mr. W. S. Hoffman of this laboratory to repeat their work to clear up the discrepancy. After several trials, he has been able to obtain the dihydroxy compound in alcohol solution by their method, but only in 20% yield, and melting, after two recrystallizations from ether, at 56° (B. and W. give 64°); sulfur, found, 36.00%, instead of calc., 35.18%. The high melting point reported above must have been due to contamination with one of the ethylene polysulfides, indicated by the high sulfur content. The melting points of

From the dihydroxy compound, the dichloride was prepared by boiling the former with several parts of conc. hydrochloric acid for an hour. The chloride separates as a yellow oil which solidifies as it cools. It was recrystallized from hot alcohol and melted at  $64^{\circ}$

Calc.: S, 29.26. Found: 29.87. Calc.: Cl, 32.36. Found: 30.99.

This shows that some of the hydroxy compound was present. It is readily hydrolyzed.

Similarly the bromide was obtained and melted at  $90-94^{\circ}$ .

Calc.: S, 20.81. Found: 21.42. Calc.: Br, 51.88. Found: 50.73.

By heating the dihydroxy compound with acetyl chloride a liquid was obtained which seemed to be the di-acetate.

### Physiological Effects

On account of the higher molecular weight, the volatility is less and the vapors would not be expected to show the activity of the monosulfide. When a tiny particle is placed on the human skin, a burn is produced, but its effect is considerably less than that of mustard gas.<sup>8</sup>

Conjunctivitis of the eyes and a rash over hands and face were suffered by the operator while working with it.

### Summary

An analog of mustard gas,  $(\text{ClCH}_2\text{CH}_2\text{SCH}_2)_2$ , m. p.  $64^{\circ}$ , has been prepared and found to have decided vesicant action. The corresponding dihydroxy compound, m. p.  $114-117^{\circ}$ , was made as an intermediate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE]

## TRihalogen-Methyl Reactions. IV. Reaction of Trichloro-acetic Acid with Copper

By Howard Waters Doughty and Benjamin Freeman

Received December 12, 1921

For several years the senior author has been interested in the behavior of compounds which contain the trichloro- or tribromo-methyl group, with copper in presence of aqueous ammonia.<sup>1,2,3</sup> With the exception of benzotrichloride, all of this class of compounds which have been tested react with copper more or less rapidly in the presence of aqueous ammonia, all our samples were indefinite. Mr. Hoffman, by the use of thionyl chloride, has obtained the crude dichloride melting at  $53^{\circ}$  agreeing well with Bennett and Whincop who give  $54^{\circ}$  as the melting point of the unrecrystallized chloride.—E. E. R.

<sup>8</sup> Our thanks for the physiological tests are due to Lt. Harry A. Kuhn, Chief of the Dept. of Toxicology, Edgewood Arsenal.

<sup>1</sup> Doughty, *THIS JOURNAL*, **39**, 2685 (1917).

<sup>2</sup> Doughty, *ibid.*, **41**, 1129 (1919).

<sup>3</sup> Doughty and Freeman, *ibid.*, **43**, 700 (1921).