



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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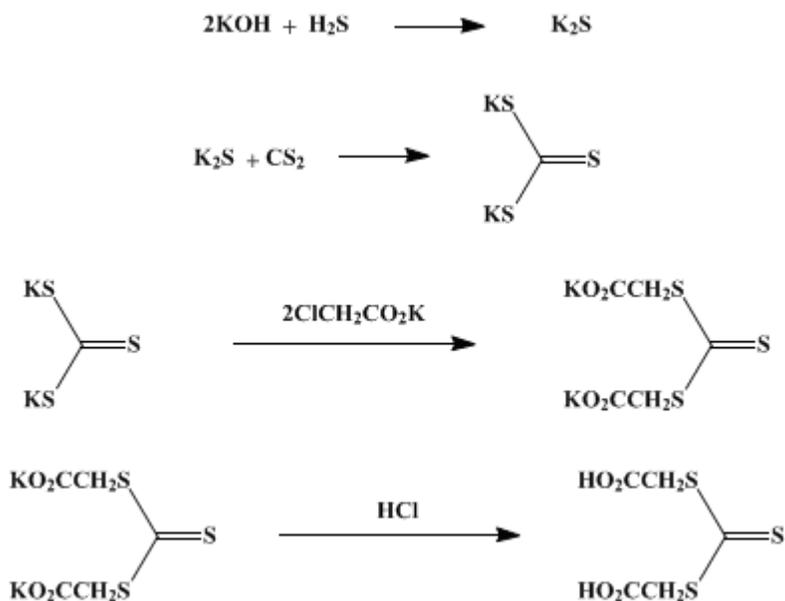
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.967 (1963); Vol. 39, p.77 (1959).

TRITHIOCARBODIGLYCOLIC ACID

[Carbonic acid, trithio-, bis[carboxymethyl] ester]



Submitted by R. E. Strube¹

Checked by John D. Roberts and Stanley L. Manatt.

1. Procedure

In a 300-ml. three-necked, round-bottomed flask equipped with a magnetic stirrer and a gas-inlet tube reaching below the surface of the liquid is placed a solution of 63 g. (0.96 mole) of [potassium hydroxide](#) (Note 1) in 100 ml. of water. The solution is cooled in ice, and [hydrogen sulfide](#) is bubbled through (Note 2) with stirring until the gain of weight is 33–34 g. (Note 3). The solution is then poured into a 3-l. three-necked, round-bottomed flask provided with a stirrer, a gas-inlet tube, a reflux condenser, and a thermometer reaching into the liquid. The small flask is rinsed with 25 ml. of ice water and the rinsings added to the rest of the solution. Then 63 g. (0.96 mole) of [potassium hydroxide](#) is added and allowed to dissolve. The 3-l. flask is then well flushed with [nitrogen](#) and, at a temperature of about 30°, 76.0 g. (1.0 mole) of [carbon disulfide](#) (Note 4) is added at once. The mixture is stirred vigorously for 2 hours (Note 5) while [nitrogen](#) is passed through at a rate of about one bubble per second (Note 6) and the temperature is kept at 35–38° (Note 7). Then the gas supply is disconnected and the dark-red solution is cooled in an ice bath.

A solution of 189 g. (2.0 moles) of [chloroacetic acid](#) (Note 8) in 300 ml. of water is neutralized to litmus with a solution containing approximately 135 g. (2.1 moles) of [potassium hydroxide](#) in 300 ml. of water. The resulting [potassium chloroacetate](#) solution is placed in a dropping funnel and added to the stirred [potassium thiocarbonate](#) solution obtained above at such a rate that the temperature does not go above 40°. After the addition is complete, the stirring is continued for 1 hour at room temperature. Then 200 ml. of concentrated [hydrochloric acid](#) is added while the temperature is kept below 20° by cooling in an ice bath. Finally, the reaction mixture is stirred for 30 minutes at room temperature. The yellow precipitate is filtered and washed twice with 150-ml. portions of ice water. The crude material is dried under reduced pressure in a vacuum desiccator over [calcium chloride](#) to constant weight (about 2 days). The drying is expedited if the lumps are occasionally broken up. The yield of yellow product having m.p. 169–174° (uncor.) (Note 9) is 152–160 g. (67–71%).

2. Notes

1. [Potassium hydroxide](#) pellets, Mallinckrodt, 85% minimum KOH assay, were used.
2. A bubbler filled with [mercury](#) was placed between the gas cylinder and the gas-inlet tube. A good hood should be used throughout the procedure because [hydrogen sulfide](#) is toxic in minute concentrations.
3. Two to three hours is required to saturate the solution. The submitter used the same 3-l. flask to prepare the [potassium sulfide](#) and to carry out the subsequent reaction. The checkers found the smaller flask more convenient for following the [hydrogen sulfide](#) uptake.
4. [Carbon disulfide](#), Mallinckrodt, analytical grade reagent, was used.
5. The [carbon disulfide](#) layer usually disappears in about 45 minutes, but longer times may be required if the stirring is not effective.
6. Contact of the reaction mixture with atmospheric [oxygen](#) is to be avoided, but the gas flow should be kept slow enough to minimize loss of [carbon disulfide](#). A bubbler filled with water was placed between the gas cylinder and the gas-inlet tube.
7. A water bath kept at 40–43°, or an electrically heated mantle may be used.
8. [Chloroacetic acid](#), m.p. 62–64°, Eastman Kodak, was used.
9. The submitter reports yields of 160–175 g. (71–77%) of product melting at 166–172°. Recrystallization from water gives 150–165 g. (66–73%) of material melting at 174–176° (cor.).

3. Discussion

Trithiocarbodiglycolic acid can be prepared by heating an aqueous solution of the alkali salts of [thiocarbonylethoxythioglycolic acid](#),^{2,3} by heating an aqueous solution of [potassium methylxanthate](#) and [sodium monochloroacetate](#),³ and by heating an aqueous solution of [potassium thiocarbonate](#) and [sodium monochloroacetate](#).³ The compound is also formed by heating an aqueous solution of [potassium ethyltrithiocarbonate](#) and [sodium monochloroacetate](#),⁴ and by heating an aqueous solution of [thiocarbonylglycolic acid-thioglycolic acid](#) with [ammonia](#)⁵ or [aniline](#).⁶ The procedure described is adapted from that of Holmberg.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 6](#)

References and Notes

1. Research Division, The Upjohn Company, Kalamazoo, Michigan.
2. Holmberg, *J. prakt. Chem.*, **71**, 271 (1905).
3. Biilmann, *Ann.*, **348**, 134 (1906).
4. Holmberg, *J. prakt. Chem.*, **75**, 182 (1907).
5. Ahlqvist, *J. prakt. Chem.*, **99**, 55 (1919).
6. Holmberg, *J. prakt. Chem.*, **84**, 645 (1911).
7. Holmberg, *J. prakt. Chem.*, **71**, 279 (1905).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

trithiocarbodiglycolic acid
[calcium chloride](#) (10043-52-4)
[hydrochloric acid](#) (7647-01-0)

ammonia (7664-41-7)

aniline (62-53-3)

hydrogen sulfide (7783-06-4)

oxygen (7782-44-7)

nitrogen (7727-37-9)

mercury (7439-97-6)

chloroacetic acid (79-11-8)

sodium monochloroacetate (3926-62-3)

potassium hydroxide (1310-58-3)

carbon disulfide (75-15-0)

potassium sulfide (1312-73-8)

potassium chloroacetate

Carbonic acid, trithio-, bis[carboxymethyl] ester (6326-83-6)

potassium thiocarbonate

thiocarbonylethoxythioglycolic acid

potassium methylxanthate

potassium ethyltrithiocarbonate

thiocarbonylglycolic acid-thioglycolic acid