Organic Syntheses

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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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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.

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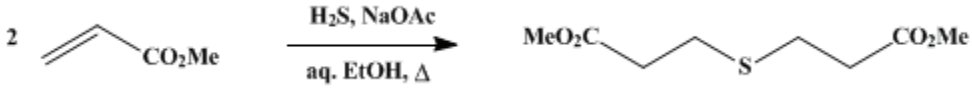
METHYL β-THIODIPROPIONATE

[Propionic acid, 3,3'-thiodi-, dimethyl ester]



Submitted by Edward A. Fehnel and Marvin Carmack[1].
Checked by Arthur C. Cope and James J. Ryan.

1. Procedure

Caution! This preparation should be conducted in a hood to avoid exposure to poisonous hydrogen sulfide.

A mixture of 150 g. (1.74 moles) of methyl acrylate (Note 1), 100 g. (0.73 mole) of sodium acetate trihydrate, and 800 ml. of 95% ethanol (Note 2) is placed in a 2-l. two-necked flask fitted with an efficient reflux condenser and a sintered-glass bubbler tube which reaches almost to the bottom of the flask. The mixture is heated on the steam bath until all the solid is dissolved and the solution is refluxing gently. A steady stream of hydrogen sulfide gas (Note 3) is introduced into the boiling solution through the bubbler tube while heating is continued for a period of 25 hours. The gas flow is then stopped, the condenser is changed for distillation, and the solvent, along with some unreacted methyl acrylate, is distilled from the mixture on the steam bath. About 200 ml. of ether and 400 ml. of water are added to the residue in the flask, and after thorough agitation the layers are separated. The aqueous layer is washed with four 50-ml. portions of ether, and the washings are added to the original ether layer. The combined ether extracts are dried over anhydrous sodium sulfate, the ether is removed by distillation on the steam bath, and the residue is distilled under reduced pressure. Methyl β-thiodipropionate is obtained as a colorless oil, b.p. 162–164°/18 mm., 138–139°/6mm.; n_D^{25} 1.4713. The yield is 128–145 g. (71–81%).

2. Notes

1. A good grade of commercial methyl acrylate containing hydroquinone is entirely satisfactory. Material of doubtful quality may be redistilled (into a receiver containing hydroquinone), b.p. 78–81°.
2. Either methanol or 95% ethanol may be used as the solvent. No ester interchange was observed to occur under the conditions employed.
3. Commercial tank hydrogen sulfide was used. The flow was regulated by passing the gas through a gas-washing bottle containing a little water. A rate of about 3–5 bubbles per second was maintained during the reaction.

3. Discussion

β-Thiodipropionic acid esters have been prepared by the addition of hydrogen sulfide to the corresponding acrylic esters in the presence of basic catalysts with [2] or without [3] solvents. The ethyl ester has also been prepared by the treatment of ethyl β-chloropropionate with sodium sulfide.[4]

References and Notes

1. University of Pennsylvania, Philadelphia, Pennsylvania.
2. I. G. Farbenind. A.-G., Fr. pat. 797,606 [*Chem. Zentr.*, **107, II**, 1062 (1936)] [*C. A.*, **30**, 8244 (1936)]; Ger. pat. 669,961 [*C. A.*, **33**, 5415 (1939)].
3. Gershbein and Hurd, *J. Am. Chem. Soc.*, **69**, 241 (1947).

4. Arndt and Bekir, *Ber.*, **63**, 2393 (1930).

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

Methyl β-thiodipropionate

ethanol (64-17-5)

methanol (67-56-1)

ether (60-29-7)

hydroquinone (123-31-9)

hydrogen sulfide (7783-06-4)

sodium sulfate (7757-82-6)

sodium sulfide (1313-82-2)

methyl acrylate (96-33-3)

sodium acetate trihydrate (6131-90-4)

ethyl β-chloropropionate (623-71-2)

Propionic acid, 3,3'-thiodi-, dimethyl ester (4131-74-2)