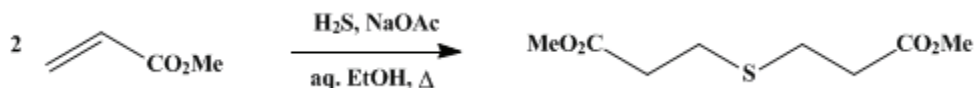


METHYL β -THIODIPROPIONATE

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



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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).

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 \$\beta\$ -chloropropionate \(623-71-2\)](#)

[Propionic acid, 3,3'-thiodi-, dimethyl ester \(4131-74-2\)](#)