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](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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.*

β-HYDROXYETHYL METHYL SULFIDE

[Ethanol, 2-methylmercapto-]

\[
\begin{align*}
\text{SCH}_3 \\
\left(\text{HN} \rightleftharpoons \text{C} \left(\text{NH}_2\right)_2\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{CH}_3\text{SH} \\
\text{CH}_3\text{SH} + \text{NaOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{SNa} + 2\text{CH}_3\text{OH} \\
\text{Cl} \text{-} \text{OH} \xrightarrow{\text{CH}_3\text{SNa}} \text{EtOH, } \Delta \rightarrow \text{CH}_3\text{S} \text{-} \text{OH}
\end{align*}
\]

Submitted by Wallace Windus and P. R. Shildneck.
Checked by H. T. Clarke and S. Gurin.

1. Procedure

A 2-l. three-necked flask is fitted with a dropping funnel, a stopcock, and a long condenser. The end
of the condenser is connected with the following assembly: a safety trap, consisting of an empty gas-
washing bottle; a second wash bottle containing 100 cc. of dilute sulfuric acid (1 volume of
concentrated sulfuric acid to 2 volumes of water); a tower, about 30 cm. high, containing calcium
chloride; an empty 2-l. flask which acts as a trap; a 2-l. flask containing 80.5 g. (3.5 gram atoms) of
clean sodium dissolved in 1.5 l. of absolute alcohol; an empty 1-l. flask and a 1-l. flask containing 500
cc. of a saturated solution of lead acetate (Note 1). The exit tube from this last flask leads to a suction
pump.

After 556 g. (2 moles) of methyl isothiourea sulfate (p. 411) is placed in the three-necked flask, a
very slow current of air is drawn through the apparatus by means of the suction pump while 800 cc. of
cold 5 N sodium hydroxide is added to the methyl isothiourea sulfate through the dropping funnel. The
mixture is warmed very slowly to generate the methyl mercaptan (Note 2). As the reaction nears
completion (after about two hours), the mixture is heated strongly for about thirty minutes (Note 3).

The solution of sodium methyl sulfide in absolute alcohol is transferred to a 3-l. three-necked flask,
which is placed on a steam bath and fitted with a dropping funnel, a reflux condenser, and a mechanical
stirrer. The solution is heated until the alcohol begins to boil. Heating is then discontinued and 302 g.
(3.75 moles) of ethylene chlorohydrin (Note 4) is added dropwise with efficient stirring over a period of
about two hours (Note 5). The reaction mixture is concentrated by distilling as much of the alcohol as
possible on the steam bath. The mixture is then allowed to cool and the sodium chloride removed by
filtration. The flask is rinsed and the sodium chloride washed with three 100-cc. portions of 95 per cent
alcohol. The combined filtrate and washings are concentrated on the steam bath under reduced pressure
until no further distillate passes over. The residue is then transferred to a modified Claisen flask and
fractionally distilled under reduced pressure. The yield is 238–265 g. (74–82 per cent of the theoretical
amount based on the sodium used) of a product boiling at 68–70°/20 mm. (Note 6).

2. Notes

1. The lead acetate removes any unreacted methyl mercaptan by precipitating it as the lead salt.
2. The rate of heating controls the rate of evolution of the methyl mercaptan. After the rapid evolution
of the gas begins, the reaction mixture should be heated very gently. The slight suction aids in obtaining
a regular flow of the gas.
3. The evolution of methyl mercaptan is almost complete after one and one-half to two hours. Prolonged vigorous heating increases the amount of ammonia evolved.

4. The ethylene chlorohydrin should be redistilled and the fraction boiling at 126–128° should be used.

5. The reaction is usually complete immediately after the addition of the ethylene chlorohydrin, obviating the necessity for refluxing the mixture. When the reaction is complete the solution is neutral to litmus paper.

6. Quantities of material five times as large as those called for above may be used without decreasing the percentage yield of product. With the larger amounts of material it is more convenient to filter the sodium chloride before concentrating the solution.

3. Discussion

The methods for preparing methyl mercaptan and β-hydroxyethyl methyl sulfide are essentially those of Arndt\(^1\) and Kirner,\(^2\) respectively.

This preparation is referenced from:


References and Notes

1. Arndt, Ber. 54, 2238 (1921).

Appendix

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

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