



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](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.

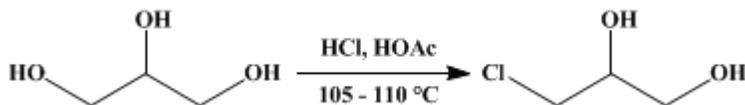
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 1, p.294 (1941); Vol. 2, p.33 (1922).*

## GLYCEROL $\alpha$ -MONOCHLOROHYDRIN

[1,2-Propanediol, 3-chloro-]



Submitted by J. B. Conant and O. R. Quayle.

Checked by O. Kamm and A. O. Matthews.

### 1. Procedure

Five hundred grams (402 cc., 4.9 moles) of 90 per cent glycerol and 10 g. of glacial acetic acid are mixed in a weighed 1-l. flask, which is placed in an oil bath heated to 105–110° (Note 1). A rapid stream of dry hydrogen chloride (Note 2) is introduced into the mixture. The flask is removed from the bath from time to time and reweighed. At the end of about four hours the flask will have gained 190 g. in weight. The reaction is then complete.

The product is distilled under reduced pressure. Below 114°/14 mm., 220–250 g. distil; this portion is mostly water. The monochlorohydrin is collected between 114° and 120°/14 mm. (Note 3), and weighs 360 g. (66 per cent of the theoretical amount) (Note 4). About 20 g. more may be obtained by neutralizing the first fraction and separating the aqueous layer.

### 2. Notes

1. The same apparatus is employed as in the preparation of glycerol  $\alpha,\gamma$ -dichlorohydrin (p. 292).
2. Two kilograms of concentrated sulfuric acid and 750 g. of concentrated hydrochloric acid are sufficient to produce the necessary amount of hydrogen chloride. See pp. 293 and 534 for the generation of hydrogen chloride.
3. The portion boiling 120–130°/14 mm. amounts to only 15–30 g., showing that very little of the  $\beta$ -compound is formed. This is further shown by the fact that the dichlorohydrin formed by continued action of hydrogen chloride under the same conditions contains very little, if any,  $\alpha,\beta$ -dichlorohydrin.
4. A light straw-colored final product is obtained in some cases.

An alternative procedure which is slower and gives slightly lower yields, but which does not require a hydrogen chloride generator, is as follows:

Three hundred grams of 90 per cent glycerol, 600 cc. of hydrochloric acid (sp. gr. 1.19), and 15 g. of glacial acetic are heated under a reflux condenser for ten hours, in a 2-l. flask. The boiling should be very gentle in the early stage of the reaction, as considerable hydrogen chloride vapor is evolved. As the reaction progresses, and the evolution of acid vapors diminishes, the mixture is more strongly heated.

The reaction products are distilled under ordinary pressure until the temperature of the liquid has reached 140° (thermometer bulb immersed in the liquid). The residual products are distilled under diminished pressure, and the following fractions obtained: (1) up to 115°/11 mm.; (2) 115–117°/11 mm.; and (3) 117–170°/11 mm. (1) is mostly aqueous hydrochloric acid; (2) is the monochlorohydrin; and (3) is glycerol. The second fraction is redistilled, and the portion boiling at 115–118°/11 mm. or 133–136°/20 mm. is collected. The yield is 190–205 g., 59–63 per cent of the theoretical amount. Higher yields are possible by reworking the residues in a procedure which is in essential accordance with that outlined.<sup>1</sup>

### 3. Discussion

Glycerol  $\alpha$ -monochlorohydrin can be prepared by the action of hydrogen chloride on glycerol<sup>2</sup> or on glycerol mixed with an equal volume of acetic acid<sup>3</sup> or other organic acid<sup>4</sup> as catalyst, or on glycerol with the ester of an organic or inorganic acid as a catalyst;<sup>5</sup> by the action of aqueous hydrochloric acid on glycerol<sup>6</sup> alone or with an organic acid (1–2 per cent), such as acetic, as a catalyst;<sup>7</sup> and by heating

epichlorohydrin with water in the presence of sulfuric acid as a catalyst.<sup>8</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 296](#)

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## References and Notes

1. Rider and Hill, *J. Am. Chem. Soc.* **52**, 1521 (1930).
2. Berthelot, *Ann.* **88**, 311 (1853); *Ann. chim. phys.* (3) **41**, 296 (1854); Sprengstoffwerke Nahnsen, Ger. pat. 254,709 and 269,657 [Frld. **11**, 30, 31 (1912–14)].
3. Reboul, *Ann. chim. phys.* (3) **60**, 18 (1860).
4. Boehringer and Sons, Ger. pat. 197,308 [Frld. **9**, 33 (1908–10)].
5. Westfälisch-Anhaltische Sprengstoff-Aktiengesellschaft, Ger. pat. 23,510 [Frld. **9**, 36 (1908–10)]; Chemische Fabrik Griesheim-Elektron, Ger. pat. 16,579 [Frld. **9**, 36 (1908–10)].
6. Deutsche Sprengstoff-Aktiengesellschaft, Ger. pat. 180,668 [Frld. **8**, 27 (1905–07)]; Norris and Milliken, *J. Am. Chem. Soc.* **42**, 2096 (1920).
7. Boehringer and Sons, Ger. pat. 197,309 [Frld. **9**, 34 (1908–10)]; Rider and Hill, *J. Am. Chem. Soc.* **52**, 1521 (1930); Fairbourne, Gibson and Stephens, *Chemistry & Industry*, **49**, 1021 (1930); Glattfeld, Leavell, Spieth and Hutton, *J. Am. Chem. Soc.* **53**, 3165 (1931).
8. Fourneau and Ribas y Marquès, *Bull. soc. chim.* (4) **39**, 699 (1926); Böeseken and Hermans, *Rec. trav. chim.* **42**, 1106 (1923).

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

ester

Glycerol  $\alpha,\gamma$ -dichlorohydrin

acetic

Glycerol  $\alpha$ -monochlorohydrin

[sulfuric acid](#) (7664-93-9)

[hydrogen chloride](#),  
[hydrochloric acid](#) (7647-01-0)

[acetic acid](#) (64-19-7)

[glycerol](#) (56-81-5)

[Epichlorohydrin](#) (106-89-8)

[1,2-Propanediol, 3-chloro-](#) (96-24-2)