



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.

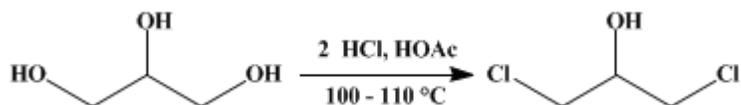
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.292 (1941); Vol. 2, p.29 (1922).

GLYCEROL α,γ -DICHLOROHYDRIN

[2-Propanol, 1,3-dichloro-]



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1. Procedure

One kilogram (805 cc., 9.8 moles) of 90 per cent glycerol (sp. gr., 1.243) and 20 g. of acetic acid are placed in a weighed 2-l. flask which is immersed in an oil bath heated to 100–110° (Note 1). The flask is fitted with a two-holed stopper, which carries a long tube reaching to the bottom of the flask and a short exit tube. The long tube is connected to a hydrogen chloride generator (Note 2); the short one, to a catch-bottle and some system for absorbing any excess of hydrogen chloride (see Fig. 7 on p. 97). A stream of dry hydrogen chloride is passed into the mixture. The absorption of gas is very rapid at the start but gradually falls off towards the end of the reaction; the stream of hydrogen chloride should be regulated accordingly. The flask is removed from time to time and weighed; when the absorption of gas practically ceases, the increase in weight will be about 875 g. (25 per cent more than the theoretical amount).

The product is now cooled, placed in a 4-l. beaker, and treated with solid sodium carbonate until just alkaline to litmus. water is added from time to time, to facilitate the reaction with the sodium carbonate and to prevent the separation of salt; about 500 cc. is required. The mixture is transferred to a separatory funnel and the aqueous layer separated. The crude dichlorohydrin, which weighs 1250 g., is distilled under reduced pressure. The first fraction boiling below 68°/14 mm. weighs 225 g., and consists of water and some dichlorohydrin; the dichlorohydrin is collected between 68° and 75°/14 mm., and weighs about 775 g. The water is separated from the first fraction, which is then redistilled and yields 100 g. of dichlorohydrin. A further amount of material (40–45 g.) may be obtained by extracting the aqueous layer obtained in the neutralization process with benzene. This is, however, hardly profitable. The neutralization and distillation will require about four hours.

The 875 g. of dichlorohydrin thus obtained boils over a 7° range; this is 70 per cent of the theoretical amount (Note 3). Redistillation yields 700–720 g. boiling at 70–73°/14 mm. (55–57 per cent of the theoretical amount).

2. Notes

- The oil bath can be conveniently heated on an electric hot plate.
- Hydrogen Chloride.*—The most convenient hydrogen chloride generator is that described by Sweeney.¹ Concentrated hydrochloric acid is introduced into concentrated sulfuric acid by means of a dropping funnel and a capillary tube leading to the bottom of the sulfuric acid container. It is convenient to use a 3-l. bottle for this container and a 1-l. funnel to contain the hydrochloric acid. The gas is dried by passing through a wash bottle containing concentrated sulfuric acid. An empty catch-flask should be connected between the generator and the absorption flask in case any glycerol tends to suck back at the start of the reaction. About 6 kg. of concentrated hydrochloric acid and 10 kg. of concentrated sulfuric acid are required in one run. The generating flask will have to be recharged every six hours; it should be half filled with sulfuric acid. Aside from this, the apparatus needs no attention. It is suggested that hydrogen chloride can be readily and conveniently prepared by dropping concentrated sulfuric acid on dry lumps of ammonium chloride (D. T. Gibson, private communication). Large quantities of hydrogen chloride can be prepared by adding concentrated sulfuric acid to a paste of sodium chloride and concentrated hydrochloric acid (see Note 1 on p. 534).

3. The dichlorohydrin boiling over a 7° range is sufficiently pure for most purposes. It contains very little, if any, isomeric dichlorohydrin, since on oxidation it gives [dichloracetone](#) (p. 211) in good yields.

3. Discussion

Glycerol α,γ -dichlorohydrin can be prepared by the action of [hydrogen chloride](#) on [glycerol](#),² on [glycerol](#) mixed with an equal volume of [acetic acid](#),³ on [glycerol](#) containing 1–2 per cent of some organic acid, as acetic, as a catalyst;⁴ by the action of aqueous [hydrochloric acid](#)⁵ or [hydrogen chloride](#)⁶ on [glycerol](#) containing [acetic acid](#) as a catalyst; and by the action of [hydrogen chloride](#) on [glycerol](#) in the presence of a water-immiscible solvent, such as [dibutyl ether](#), and at a temperature such that steam distillation takes place.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 5](#)
- [Org. Syn. Coll. Vol. 1, 166](#)
- [Org. Syn. Coll. Vol. 1, 211](#)
- [Org. Syn. Coll. Vol. 1, 233](#)
- [Org. Syn. Coll. Vol. 1, 237](#)
- [Org. Syn. Coll. Vol. 1, 294](#)
- [Org. Syn. Coll. Vol. 1, 314](#)
- [Org. Syn. Coll. Vol. 1, 364](#)
- [Org. Syn. Coll. Vol. 1, 377](#)
- [Org. Syn. Coll. Vol. 1, 451](#)
- [Org. Syn. Coll. Vol. 1, 533](#)
- [Org. Syn. Coll. Vol. 2, 256](#)
- [Org. Syn. Coll. Vol. 2, 284](#)
- [Org. Syn. Coll. Vol. 4, 169](#)
- [Org. Syn. Coll. Vol. 4, 238](#)
- [Org. Syn. Coll. Vol. 4, 605](#)

References and Notes

1. Sweeney, *J. Am. Chem. Soc.* **39**, 2186 (1917).
2. Berthelot, *Ann.* **88**, 311 (1853); *Ann. chim. phys.* (3) **41**, 297 (1854); Fauconnier and Sanson, *Bull. soc. chim.* (2) **48**, 237 (1887); Bigot, *Ann. chim. phys.* (6) **22**, 437 (1891); *Chemische Fabrik von Heyden*, Ger. pat. 263,106 [Fr. **11**, 32 (1912–14)]; Grün, Ger. pat. 272,337 [Fr. **11**, 33 (1912–14)]; Smith, *Z. physik. Chem.* **92**, 717 (1918), **93**, 59 (1919), **94**, 691 (1920).
3. Reboul, *Ann. Spl.* **1**, 218 (1861); *Ann. chim. phys.* (3) **60**, 18 (1860).
4. Boehringer and Sons, Ger. pat. 197,308 [Fr. **9**, 33 (1908–10)].
5. Boehringer and Sons, Ger. pat. 197,309 [Fr. **9**, 34 (1908–10)].
6. Hill and Fischer, *J. Am. Chem. Soc.* **44**, 2587 (1922); Fairbourne, Gibson and Stephens, *Chemistry & Industry* **49**, 1021 (1930) [C. A. **25**, 915 (1931)].
7. Dow Chemical Co., U. S. pat. 2,144,612 [C. A. **33**, 2914 (1939)].

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

Glycerol α,γ -dichlorohydrin

acetic

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ammonium chloride (12125-02-9)

glycerol (56-81-5)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

dichloroacetone (513-88-2)

2-Propanol, 1,3-dichloro- (96-23-1)

dibutyl ether (142-96-1)