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.

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.

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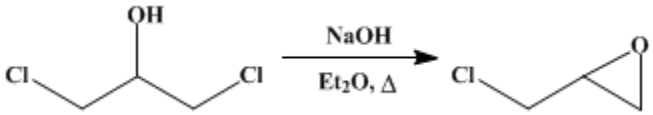
Organic Syntheses, Coll. Vol. 1, p.233 (1941); Vol. 3, p.47 (1923).

EPICHLOROHYDRIN



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Checked by Roger Adams and H. O. Calvery.

1. Procedure

In a 5-l. flask (Note 1) provided with a mechanical stirrer, a reflux condenser, and a hopper which can be opened or closed at the bottom by means of a rubber bung attached to a glass rod (Fig. 12), are placed 3 l. of anhydrous ether and 1290 g. (943 cc., 10 moles) of glycerol α,γ-dichlorohydrin (p. 292). The flask is surrounded by a cold-water bath, and 440 g. (11 moles) of finely powdered sodium hydroxide (Note 2), which has been passed through a 20-mesh sieve, is added through the hopper in small portions, with continual stirring, while the temperature is kept at 25–30°. The addition requires about twenty minutes. The cold water is replaced by water at 40–45°, and the mixture boiled gently with stirring for four hours. It is necessary to cool the vessel at least once every hour during this period and break up with a rod or wire any lumps which cling to the side of the flask and are not incorporated by the stirrer.

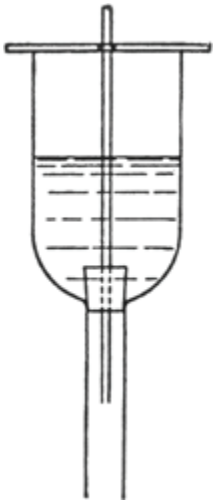

Fig. 12.

The mixture is finally cooled and the ethereal solution carefully decanted from the solid, which is carefully rinsed twice with 250-cc. portions of dry ether. The united liquids are then distilled from a water bath held at 46–60°, the residue is fractionated with a column, and the fractions boiling at the following points are collected: up to 110°; at 110–115°; at 115–117°; and at 117–140°. The portion boiling at 115–117° is pure epichlorohydrin; the lower and higher fractions are systematically redistilled, yielding a further quantity of pure material. The yield is 705–747 g. (76–81 per cent of the theoretical amount). The residue, varying from 16 to 150 g., consists of nearly pure glycerol dichlorohydrin, and may be employed in subsequent runs (Note 3).

2. Notes

1. A three-necked flask is very satisfactory for this reaction; if it is not available, the tubes leading from the reflux condenser and the hopper must be bent at slight angles to prevent congestion of apparatus.
2. The principal difficulties in the preparation are connected with the use of finely powdered alkali. Care must be taken to expose the powder as little as possible to a moist atmosphere, for if it becomes at all damp it tends to clump together and difficulty is experienced in adding it to the mixture. For this reason, and also on account of the irritating action of alkali on the mucous membranes, the sieve should be provided with well-fitting cover and receiver; the sifted material should be weighed out into a stoppered bottle and placed in the apparatus directly from this container. The hopper (Fig. 12) from which the alkali is added to the mixture should be covered with a card with a hole through which the rod passes. The bung on the rod may conveniently be constructed from a rubber stopper of appropriate size.
3. It is not essential to redistil the recovered dichlorohydrin, since the glycerol which forms the principal by-product is retained by the excess alkali and does not enter the ether.

3. Discussion

Epichlorohydrin can be prepared by the action of alkalies on glycerol α- and β-dichlorohydrins.[1] An alternative procedure involving the use of calcium hydroxide has also been described.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 256
- Org. Syn. Coll. Vol. 4, 10

References and Notes

1. Claus, Ber. **10**, 557 (1877); Reboul, Ann. Suppl. **1**, 221 (1861); Münder and Tollens, Z. Chem. 252 (1871); Prevost, J. prakt. Chem. (2) **12**, 160 (1875); Fairbourne, Gibson and Stephens, Chemistry and Industry **49**, 1021 (1930) [C. A. **25**, 915 (1931)].
2. Griesheim, Ger. pat. 246,242 [Frdl. **10**, 22 (1910–1912)]; Braun, J. Am. Chem. Soc. **54**, 1248 (1932); Org. Syn. **16**, 30.

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

Glycerol α,γ-dichlorohydrin

glycerol dichlorohydrin

glycerol α- and β-dichlorohydrins

ether (60-29-7)

sodium hydroxide (1310-73-2)

glycerol (56-81-5)

Epichlorohydrin (106-89-8)

calcium hydroxide