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.

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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.

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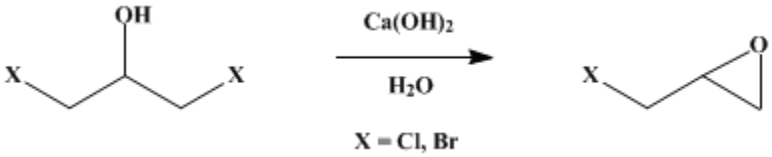
Organic Syntheses, Coll. Vol. 2, p.256 (1943); Vol. 16, p.30 (1936).

EPICHLOROHYDRIN AND EPIBROMOHYDRIN



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1. Procedure

(*A*) *Epichlorohydrin*.—In a 5-l. round-bottomed flask, 1350 g. (988 cc., 10.5 moles) of glycerol α,γ-dichlorohydrin (Org. Syn. Coll. Vol. I, **1941**, 292), 840 g. (10 moles) of technical, finely powdered calcium hydroxide (88 per cent), and 840 cc. of water (20°) are shaken vigorously for fifteen minutes (Note 1). The mixture forms a thick paste at the beginning, but the epichlorohydrin soon separates from the calcium salts as a mobile liquid. The flask is fitted with a rubber stopper carrying a wide delivery tube, and the mixture is distilled from a water bath, at first under 40–50 mm. pressure. The pressure is then lowered to 10 mm. and the temperature raised gradually to 95–100° (Note 2). The receiver must be cooled effectively in an ice-salt mixture to −5° or below, to ensure a maximum yield. The distillate is transferred to a separatory funnel, the upper, aqueous, layer returned to the reaction flask, and the distillation repeated. A third distillation in a similar manner gives a small additional amount of epichlorohydrin (Note 3). The lower layers from the successive distillations are combined and distilled through a fractionating column, under reduced pressure. The epichlorohydrin fraction is collected up to 75°/50 mm., and the residue (about 160–180 cc.), which contains a large percentage of dichlorohydrin, is returned to the original reaction flask, together with 150 cc. of water. This material is distilled once under reduced pressure as described above, and the lower layer of the distillate is combined with the main fraction of epichlorohydrin. The crude product is distilled at ordinary pressure until the temperature of the vapor reaches 115°; at this point the distillation is stopped and the water layer removed from the distillate. The lower layer of the distillate is dried over anhydrous sodium sulfate and returned to the distilling flask. After a small fore-run, the epichlorohydrin distils at 115–117°. The yield is 650–700 g. (67–72 per cent of the theoretical amount).

(*B*) *Epibromohydrin*.—In a 5-l. round-bottomed flask, 2140 g. (1 l., 9.8 moles) of glycerol α,γ-dibromohydrin (p. 308) is suspended in 1.5 l. of water, and 400 g. of technical, powdered calcium hydroxide (88 per cent) is added gradually, with shaking, in the course of about fifteen minutes. A further 400 g. of calcium hydroxide (total, 9.5 moles) is added at once, and the epibromohydrin is distilled at reduced pressure in the manner described for epichlorohydrin (Note 2). The combined lower layers from two such distillations (about 750 cc.) are dried over anhydrous sodium sulfate and fractionated at atmospheric or reduced pressure. The yield of epibromohydrin, b.p. 134–136° or 61–62°/50 mm., is 1130–1200 g. (84–89 per cent of the theoretical amount).

2. Notes

1. The prescribed amount of water should be used; more water causes frothing. The reaction is not exothermic.
2. Epichlorohydrin boils at 30–32°/10 mm., epibromohydrin at 61–62°/50 mm. Both these liquids are quite volatile with water vapor under reduced pressure.
3. The volume of the epichlorohydrin layer obtained in the successive distillations is roughly: (1) 500 cc., (2) 200 cc., (3) 20 cc.

3. Discussion

Epichlorohydrin[1] and epibromohydrin[2] have been prepared by treatment of glycerol dichloro- and

dibromohydrins with alkalies in various ways. The procedures described here represent a laboratory application of the Griesheim process.[3]

References and Notes

1. Org. Syn. Coll. Vol. I, **1941**, 233.
2. Berthelot and Luca, Ann. chim. (3) **48**, 306, 311 (1856); Reboul, ibid. (3) **60**, 32 (1860).
3. Chemische Fabrik Griesheim-Elektron, Ger. pat. 246,242 [Frdl. **10**, 22 (1910–12)]; Braun, J. Am. Chem. Soc. **54**, 1248 (1932).

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

Glycerol α,γ-dichlorohydrin

Glycerol α,γ-dibromohydrin

glycerol dichloro- and dibromohydrins

Epichlorohydrin (106-89-8)

sodium sulfate (7757-82-6)

calcium hydroxide

Epibromohydrin (3132-64-7)