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.

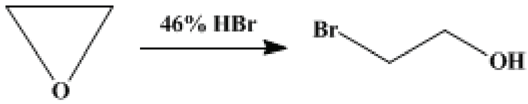
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.006.0012

Organic Syntheses, Coll. Vol. 1, p.117 (1941); Vol. 6, p.12 (1926).

2-BROMOETHANOL

[Ethanol, 2-bromo-]

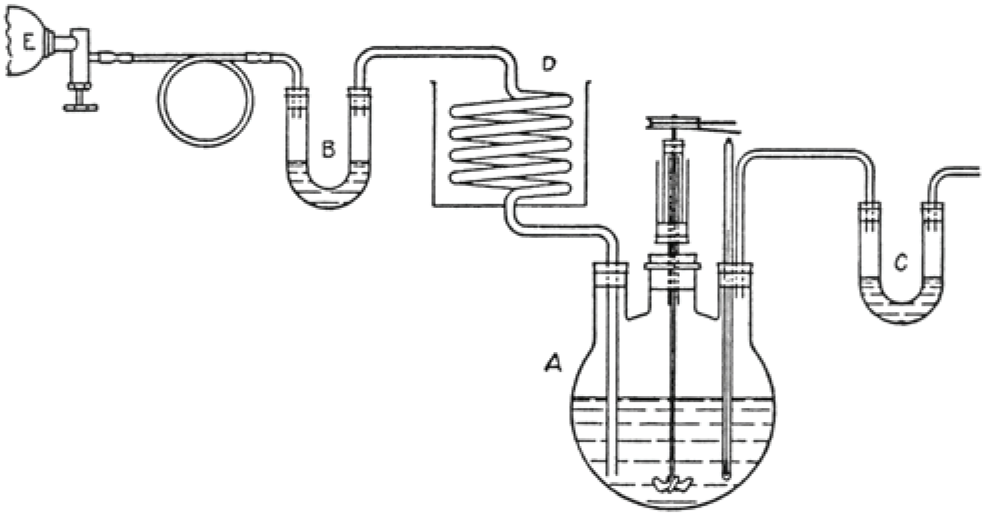


Submitted by F. K. Thayer, C. S. Marvel, and G. S. Hiers.
Checked by Henry Gilman and F. Schulze.

1. Procedure

In the 1-l. three-necked flask A (Fig. 8) is placed 550 cc. (4.56 moles) of 46 per cent hydrobromic acid (sp. gr. 1.46) (Note 1). Ethylene oxide (Note 2) is led into the acid solution as indicated in Fig. 8. The tank E is arranged on a balance so that the amount of ethylene oxide which is used can be weighed. B is a U-tube containing water to indicate the rate of flow of the gas. D is a glass coil surrounded by ice and salt which cools the gas nearly to the liquefaction temperature. C is another U-tube containing water which shows whether or not the gas is being completely absorbed.

Fig. 8.



The flask A is surrounded by an ice-salt bath and the stirrer is started. When the temperature of the acid has dropped to 10°, 132 g. (3 moles) of ethylene oxide is added over a period of about two and one-half hours (Note 3). The stirring is continued for one hour (Note 4) after all of the ethylene oxide has been added and the temperature is maintained below 10° during the reaction.

After this time the excess hydrobromic acid is neutralized with excess sodium carbonate, of which about 100 g. of anhydrous salt is required. To the aqueous solution is then added about 100 g. of anhydrous sodium sulfate until some of the solid does not dissolve. A layer of ethylene bromohydrin separates and is collected in 200 cc. of ether. The ether layer is below the aqueous layer. The solid sodium sulfate is filtered from the solution and washed once or twice with a small amount of ether (Note 5) to remove any mechanically held bromohydrin. The aqueous filtrate is twice extracted with 200-cc. portions of ether (Note 6). The combined ether extracts are dried overnight with anhydrous sodium sulfate, filtered and distilled from a steam bath (Note 7). The remaining bromohydrin is distilled under reduced pressure (Note 8). After two distillations the fraction boiling at 55–59°/22 mm. (Note 9) is pure ethylene bromohydrin. The yield is 327–345 g. (87–92 per cent of the theoretical amount).

2. Notes

1. An equivalent amount of hydrobromic acid of greater strength may be used. Acid of lower concentration gives a much lower yield. The preparation of 48 per cent hydrobromic acid is described on p. 26.

2. Ethylene oxide attacks rubber very rapidly. Hence if rubber is used to connect the glass tubes which conduct the gas to the reaction flask, care must be taken to have the glass tubes meet inside the rubber tubing.

Undue exposure to ethylene oxide should be avoided because of its toxicity.

3. The ethylene oxide must be added quite rapidly in order to complete the addition in the time specified. It should be added at a maximum possible rate consistent with practically no loss of ethylene oxide through tube C. The best absorption of ethylene oxide appears to take place when the temperature is kept between 0° and 10°. Absorption cannot be complete in two and one-half hours when the temperature is kept at 0°.

4. When the mixture is stirred too long or the temperature is allowed to rise much above 10° the yields are lower.

5. The ether used to wash the sodium sulfate crystals may be used for the extraction of the aqueous solution.

6. When the bromohydrin is removed by the first treatment with ether, the ethereal layer is on the bottom. Subsequent ethereal extractions float on the aqueous layer.

7. About 300–335 cc. (50–55 per cent) of ether is recovered.

8. A modified Claisen flask (p. 130) is used to fractionate the compound. Distillation under atmospheric pressure causes some decomposition.[1]

9. In the first distillation the fraction boiling at 50–65°/22 mm. is collected. Boiling points observed at other pressures are as follows: 47–51°/15 mm.; 59–63°/25 mm.; and 90–94°/80 mm.

3. Discussion

Ethylene bromohydrin can be prepared by the reaction between ethylene glycol and hydrobromic acid[2] and phosphorus tribromide;[3] by the direct addition of hypobromous acid to ethylene;[4] and by the reaction between ethylene and dilute bromine water.[5] With ethylene oxide now available at a reasonable price, the procedure described has been selected because of the high yields and the convenience of reaction.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 314
- Org. Syn. Coll. Vol. 1, 528

References and Notes

1. Read and Williams, J. Chem. Soc. **117**, 1216 (1920).
2. Henry, Jahresber. 304 (1872); Norris, Watt and Thomas, J. Am. Chem. Soc. **38**, 1079 (1916); Karvonen, Acad. Sci. Fennicae, **5**A, 1–103 (1914) [C. A. **14**, 2176 (1920)].
3. Demole, Ber. **9**, 48 (1876).
4. Mokievsky, J. Russ. Phys. Chem. Soc. **30**, 900 (1898) [Chem. Zentr. I, 591 (1899)].
5. Read and Williams, J. Chem. Soc. **111**, 241 (1917); **117**, 359 (1920); Read and Hook, ibid. **117**, 1214 (1920); McDowall, ibid. **129**, 499 (1926).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

bromine water

ether (60-29-7)

HYDROBROMIC ACID (10035-10-6)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

phosphorus tribromide (7789-60-8)

2-BROMOETHANOL,
Ethanol, 2-bromo-,
ethylene bromohydrin (540-51-2)

Ethylene oxide (75-21-8)

ethylene glycol (107-21-1)

hypobromous acid (13517-11-8)

ethylene (9002-88-4)