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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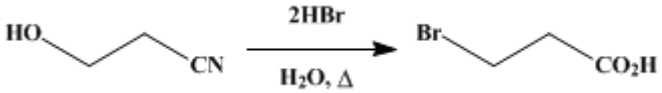
Organic Syntheses, Coll. Vol. 1, p.131 (1941); Vol. 3, p.25 (1923).

β-BROMOPROPIONIC ACID

[Propionic acid, β-bromo-]



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1. Procedure

To 2750 g. (2 l., 13.6 moles) of 40 per cent hydrobromic acid (Note 1) in a 3-l. flask is added 317 g. (4.5 moles) of ethylene cyanohydrin (p. 256), and the mixture is boiled for two hours under a reflux condenser. The condenser is then arranged for downward distillation and a thermometer immersed in the reaction mixture; dilute hydrobromic acid is distilled off until the temperature in the flask reaches 121°, whereupon the receiver is changed and a fraction consisting of stronger hydrobromic acid is collected over the range 121–129°. When the temperature of the mixture reaches 129°, very little hydrobromic acid remains, and on cooling, the mass sets to an almost colorless solid. This is now dissolved in 2000 cc. of carbon tetrachloride (Note 2), and the ammonium bromide is filtered off and washed with 500 cc. more of the solvent; a thin aqueous layer is separated and 1500 cc. of the carbon tetrachloride distilled from the filtrate. On cooling, about 470 g. of β-bromopropionic acid crystallizes from the residue; on filtering and drying, this melts at 62.5–63.5°. With further concentration, the mother liquor yields a second crop of β-bromopropionic acid, amounting to 60–70 g.

The aqueous layer separated from the main carbon tetrachloride solution is shaken with 100 cc. of carbon tetrachloride, and thus yields about 10 g. of pure acid; when the dilute and the concentrated hydrobromic acid fractions are extracted in the same way, about 5 g. and 15 g. respectively of β-bromopropionic acid are obtained. The total yield is 560–570 g. (82–83 per cent of the theoretical amount).

2. Notes

1. The 2 l. (2750 g.) of 40 per cent hydrobromic acid may advantageously be replaced by a corresponding quantity (1550 cc.) of constant-boiling 48 per cent hydrobromic acid, should this be available. Directions for the preparation of hydrobromic acid are given on p. 26.
2. In no case should benzene be used in place of carbon tetrachloride, as it has been found impossible to separate this solvent from β-bromopropionic acid, even on repeated fractionation with an efficient column.

3. Discussion

β-Bromopropionic acid can be prepared by the action of hydrobromic acid on acrylic acid,[1] on hydracrylic acid,[2] and on ethylene cyanohydrin;[3] and by the oxidation of β-bromopropionaldehdye[4] and of trimethylene bromohydrin[5] with nitric acid.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 246

References and Notes

1. Linnemann, Ann. **163**, 96 (1872); Kowski, Ann. **342**, 127 (1905).

2. Beekurts and Otto, Ber. **18**, 227 (1885).
3. Jacobs and Heidelberger, J. Am. Chem. Soc. **39**, 1466 (1917).
4. Ledever, J. prakt. Chem. (2) **42**, 384 (1890); Moureu, Bull. soc. chim. (3) **9**, 388 (1893).
5. Rojahn, Ber. **54**, 3117 (1921).

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

β-bromopropionaldehdye

Benzene (71-43-2)

nitric acid (7697-37-2)

ammonium bromide (12124-97-9)

HYDROBROMIC ACID (10035-10-6)

trimethylene bromohydrin (627-18-9)

carbon tetrachloride (56-23-5)

β-Bromopropionic acid,
Propionic acid, β-bromo- (590-92-1)

Ethylene cyanohydrin (109-78-4)

Acrylic acid (9003-01-4)

hydracrylic acid (503-66-2)