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.

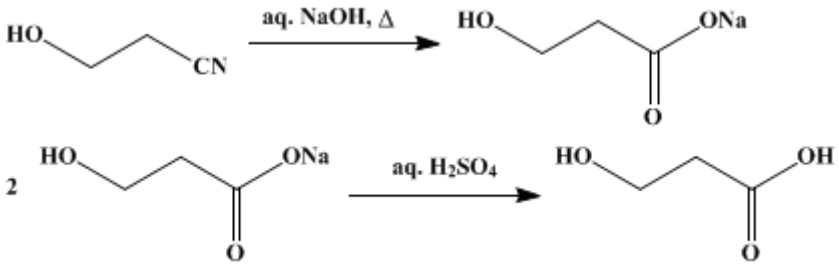
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.007.0054

Organic Syntheses, Coll. Vol. 1, p.321 (1941); Vol. 7, p.54 (1927).

β-HYDROXYPROPIONIC ACID

[Hydracrylic acid]



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1. Procedure

To a cold solution of 160 g. (4 moles) of sodium hydroxide in 500 cc. of water in a 2-l. round-bottomed flask provided with a mechanical stirrer is added slowly 250 g. (3.5 moles) of ethylene cyanohydrin (p. 256), the temperature being kept below 30° (Note 1) by means of a cold water bath. The mixture is allowed to stand overnight in the bath, when the flask is fitted with a two-holed rubber stopper bearing a capillary tube reaching almost to the bottom and a delivery tube bent slightly downward for attachment to a suction pump. The flask is then heated slowly to 80° during four hours by raising the temperature of the surrounding water. A rapid current of air is drawn through the mixture during the heating. The mixture is now evaporated to dryness under reduced pressure by heating in an oil bath, the temperature of which is raised as rapidly as the boiling of the material will permit. The oil bath is finally held at 125° until the product becomes pasty. The flask is allowed to cool, and 50 cc. of water is poured down one side of the flask, and the solid material at that point worked carefully into a paste with a stout stirring rod.

A cooled mixture of 200 g. (109 cc.) of concentrated sulfuric acid (2 moles) and 300 cc. of water is now added slowly with careful cooling (Note 2), the pasty mixture being stirred with a thermometer and the temperature not being allowed to rise above 35°. Sodium sulfate crystallizes during this addition. The mass is now shaken vigorously with 400 cc. of ether and allowed to stand for some minutes. The ether is then decanted as completely as possible and the residue filtered with suction. The sodium sulfate is now shaken with six successive 300-cc. portions of ether, the ether solutions being subsequently employed for extraction of the filtrate. This latter requires 10–14 such extractions (each with 300–400 cc. of ether) for the satisfactory extraction of the β-hydroxypropionic acid. The combined ethereal solution is dried over 50 g. of anhydrous sodium sulfate and the ether distilled from a water bath, the temperature of which is not allowed to rise above 50°. The product is then concentrated under reduced pressure from a water bath maintained at 55–60°. The residue should have attained constant weight after four to six hours of this treatment; it consists of a sirupy liquid of pale straw color which contains 75–80 per cent of β-hydroxypropionic acid (by titration) (Note 3). The yield is 120–125 g. (28–31 per cent of the theoretical amount).

2. Notes

1. If the temperature of the mixture of nitrile and sodium hydroxide is allowed to rise too soon or too rapidly, the evolution of ammonia may become almost explosive, as the reaction is strongly exothermic.
2. The temperature during the addition of the sulfuric acid must be carefully controlled, as the heat of neutralization is sufficient to decompose the product. The use of a minimum amount of water is desirable in order to decrease the number of extractions.
3. β-Hydroxypropionic acid is an uncrystallizable and hygroscopic sirup. The 20–25 per cent of impurity remaining in the final product is largely water.

3. Discussion

β-Hydroxypropionic acid can be prepared by the hydrolysis of β-bromopropionic acid;[1] by the action of alkali on acrylic acid;[2] and by the hydrolysis of ethylene cyanohydrin with acid[3] or preferably with alkali.[4]

References and Notes

1. Lossen, Ann. **342**, 128 (1905).
2. Linnemann, Ber. **8**, 1095 (1875); Erlenmeyer, Ann. **191**, 281 (1878).
3. Erlenmeyer, Ann. **191**, 269 (1878).
4. Wislicenus, Ann. **128**, 6 (1863).

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

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

β-Bromopropionic acid (590-92-1)

Ethylene cyanohydrin (109-78-4)

Acrylic acid (9003-01-4)

hydracrylic acid,
β-Hydroxypropionic acid (503-66-2)