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.

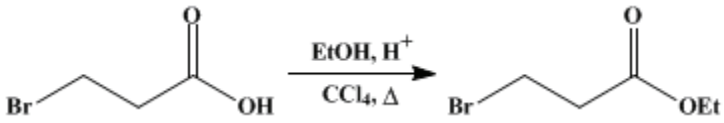
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.003.0051

Organic Syntheses, Coll. Vol. 1, p.246 (1941); Vol. 3, p.51 (1923).

ETHYL β-BROMOPROPIONATE

[Propionic acid, β-bromo-, ethyl ester]



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1. Procedure

To the crude mixture of ammonium bromide and β-bromopropionic acid, prepared as described on p. 131, from 317 g. of ethylene cyanohydrin, are added 1200 cc. of carbon tetrachloride (Note 1) and 200 cc. of the same solvent which has been shaken with the aqueous distillates; the ammonium bromide is filtered off and washed with 200 cc. of carbon tetrachloride. The watery layer, amounting to about 350 cc., is separated and shaken with 100 cc. of carbon tetrachloride. To the united carbon tetrachloride solutions are added 450 cc. of 95 per cent ethyl alcohol and 10 g. of sulfosalicylic acid or phenolsulfonic acid to act as a catalyst (Note 2).

The mixture is now boiled in a 3-l. flask, the vapors being passed through an efficient condenser and the condensed liquid run into an automatic separator (p. 422) so arranged that the heavy liquid is returned to the flask and the lighter aqueous liquid discarded. If the boiling is sufficiently vigorous no more water will separate after two to two and one-half hours' boiling (Note 3). The reaction mixture is now cooled, washed with dilute sodium carbonate solution, and distilled with the use of a column until the temperature of the vapor reaches 85° and that of the liquid in the flask about 115°. The residue is then transferred to a flask provided with a column for distillation under reduced pressure (Fig. 9, p. 130) and distilled. The fraction boiling at 60–65°/15 mm. is collected, 690–700 g. of pure ethyl β-bromopropionate being obtained (85–87 per cent of the theoretical amount). A high-boiling residue, probably consisting of ethyl hydracrylate, remains in the flask, but the amount is practically negligible.

2. Notes

1. As in the preparation of the β-bromopropionic acid (p. 131), benzene must not be substituted for the carbon tetrachloride, as it has been found impossible to make a satisfactory separation of this solvent from the ester.
2. The esterification may be carried out without the addition of a sulfonic acid, as traces of hydrobromic acid generally remain in the crude material; but since the time of operation must be kept as short as possible this omission is not recommended. It has been found that, if the water is not removed and the mixture boiled under a reflux condenser for two hours before the distillate is passed through the automatic separator, the yield falls to 70–75 per cent of the theoretical amount.
3. It is important to carry out the esterification as rapidly as possible in order to cut down to a minimum the formation of ethyl hydracrylate, which takes place by the action of water on the β-bromopropionic acid or ester; an efficient condenser is therefore necessary. For the same reason it is necessary to remove all residual water from the mixture before adding the alcohol.

3. Discussion

Ethyl β-bromopropionate can be prepared by the esterification of β-bromopropionic acid,[1] and by the addition of hydrogen bromide to ethyl acrylate.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 262

References and Notes

1. Lederer, J. prakt. Chem. (2) **42**, 384 (1890); Barthe, Compt. rend. **118**, 1268 (1894).
2. Org. Syn. **20**, 64.

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

ester

sulfonic acid

ethyl alcohol,
alcohol (64-17-5)

Benzene (71-43-2)

ammonium bromide (12124-97-9)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)

carbon tetrachloride (56-23-5)

β-Bromopropionic acid (590-92-1)

Ethylene cyanohydrin (109-78-4)

Ethyl β-bromopropionate,
Propionic acid, β-bromo-, ethyl ester (539-74-2)

sulfosalicylic acid

phenolsulfonic acid

ethyl hydracrylate (687-47-8)

ethyl acrylate (140-88-5)