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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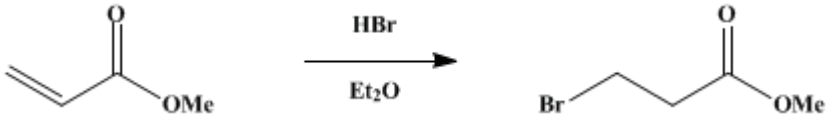
Organic Syntheses, Coll. Vol. 3, p.576 (1955); Vol. 20, p.64 (1940).

METHYL β-BROMOPROPIONATE

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



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1. Procedure

Six hundred and fifty grams of a 60% solution of methyl acrylate in methanol to which has been added 4 g. of hydroquinone (Note 1) is washed, successively, with 800-ml., 400-ml., and 200-ml. portions of a 7% sodium sulfate solution. The methyl acrylate layer is dried by shaking with 45 g. of anhydrous sodium sulfate for 20–30 minutes. The ester is then removed from the sodium sulfate by filtration and used without distillation. The yield is 280–325 g.

A solution of 258 g. (3 moles) of washed and dried methyl acrylate in 500 ml. of anhydrous ether is placed in a 1-l. round-bottomed flask. The flask is fitted with a rubber stopper carrying a drying tube and an 8-mm. glass inlet tube for hydrogen bromide. The inlet tube, which extends almost to the bottom of the flask, is connected through a 1-l. safety trap to a hydrogen bromide generator (Note 2). The flask with its contents is placed in an ice bath, and 245 g. (3.03 moles) of anhydrous hydrogen bromide is passed into the solution (Note 3). After the hydrogen bromide has been added, the flask is stoppered and allowed to stand for about 20 hours at room temperature.

The ether is removed by distillation (Note 4) from a hot-water bath. At the end of the distillation, the water bath is heated to 80–85°, and when no more liquid comes over at this temperature the residue is transferred to a 500-ml. modified Claisen distilling flask and distilled under reduced pressure. The methyl β-bromopropionate distils at 64–66°/18 mm. and weighs 410–428 g. (80–84%) (Note 5) and (Note 6).

2. Notes

1. Methyl acrylate in methanol is available from Rohm and Haas Company, Philadelphia, Pennsylvania. Since the ester polymerizes in the presence of peroxides, it is necessary to add some hydroquinone as an inhibitor. The ester should not be stored for long periods of time, even when it contains hydroquinone. Storage should be in a refrigerator.
2. The hydrogen bromide [*Org. Syntheses* Coll. Vol. 2, 338 (1943)] may be completely freed from bromine by bubbling it through a solution of phenol in carbon tetrachloride.
3. The addition may be as rapid as is convenient without the loss of ether due to the exothermic reaction.
4. The ether may be removed under anhydrous conditions and used for a subsequent preparation of the ester without further treatment.
5. Ethyl β-bromopropionate may be prepared in the same manner in about 90% yield. The boiling point of the ethyl ester is 77–79°/19 mm.
6. The residue consists largely of β-bromopropionic acid which may be recovered by distillation, b.p. 115–120°/18 mm., followed by recrystallization from carbon tetrachloride. The yield of this acid has never been more than 5% of the theoretical amount.

3. Discussion

Methyl β-bromopropionate has been prepared by the esterification of β-bromopropionic acid with methyl alcohol alone[1] and through the use of hydrogen bromide as a catalyst,[2] and by the direct addition of hydrogen bromide to methyl acrylate.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 338

References and Notes

1. Le Mer and Kamner, *J. Am. Chem. Soc.*, **53**, 2833 (1931).
2. Moureu, Murat, and Tampier, *Ann. chim.*, **15**, 221 (1921).

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

methyl alcohol,
methanol (67-56-1)

ether (60-29-7)

hydroquinone (123-31-9)

phenol (108-95-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

carbon tetrachloride (56-23-5)

β-Bromopropionic acid (590-92-1)

Ethyl β-bromopropionate (539-74-2)

methyl acrylate (96-33-3)

METHYL β-BROMOPROPIONATE,
Propionic acid, β-bromo-, methyl ester (3395-91-3)

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