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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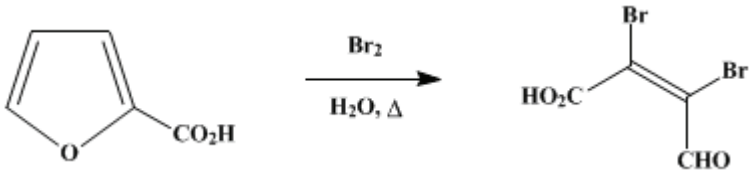
MUCOBROMIC ACID

[Acrylic acid, α,β-dibromo-β-formyl-]



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1. Procedure

In a 2-l. three-necked round-bottomed flask, equipped with a reflux condenser attached to a gas trap, a dropping funnel, and a mechanical stirrer, are placed 100 g. (0.9 mole) of furoic acid (Note 1) and 440 ml. of water. The flask is immersed in a pan of crushed ice, and 686 g. (220 ml., 4.3 moles) of bromine is placed in the dropping funnel. The stirrer is started, and the bromine is added over a period of about 1 hour with constant stirring and cooling (Note 2). The bromine is decolorized almost immediately at first and then more slowly as the reaction proceeds. The mixture is then heated to boiling and refluxed for 30 minutes. The condenser is removed and the boiling continued for an additional 30 minutes with one neck of the flask open. The mixture is cooled and chilled thoroughly, whereupon the mucobromic acid separates and is collected on a filter. The filter cake is removed and thoroughly triturated with a solution of 5 g. of sodium bisulfite in 150 ml. of water (Note 3), and the product is again removed by filtration. After drying in the air the crude product weighs 155–170 g. (67–73%) and melts at 120–122° (cor.).

The mucobromic acid may be recrystallized by solution in 250 ml. of boiling water with the addition of 2 g. of Darco. The hot solution is filtered, and the filtrate is thoroughly chilled in an ice bath. After filtration and drying there is obtained 148–155 g. (64–67%) of white crystals melting at 123–124° (cor.).

2. Notes

1. The furoic acid may be obtained from furfural by means of the Cannizzaro reaction[1] or by oxidation with alkaline potassium permanganate.[2] It is important to purify the furoic acid to a melting point of 131–132°.
2. It is essential that the flask and its contents be well cooled; otherwise the yield is materially decreased.
3. The sodium bisulfite solution removes the color produced by the excess bromine.

3. Discussion

The only practical methods of preparation are the action of bromine on furfuraldehyde[3] or furoic acid[4,5,6] in aqueous solution.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 688

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 276 (1941).

2. Wagner and Simons, *J. Chem. Education*, **13**, 270 (1936).
3. Simonis, *Ber.*, **32**, 2085 (1899).
4. Jackson and Hill, *Am. Chem. J.*, **3**, 41 (1881–2); *Ber.*, **11**, 1671 (1878).
5. Schmelz and Beilstein, *Ann. Suppl.*, **3**, 276 (1864).
6. Limpricht, *Ann.*, **165**, 293 (1873).

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

potassium permanganate (7722-64-7)

bromine (7726-95-6)

sodium bisulfite (7631-90-5)

furoic acid (88-14-2)

Furfural,
furfuraldehyde (98-01-1)

Mucobromic acid,
Acrylic acid, α,β-dibromo-β-formyl- (488-11-9)