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.

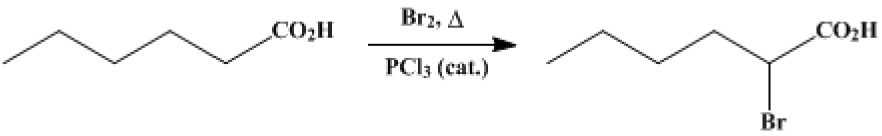
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.004.0009

Organic Syntheses, Coll. Vol. 1, p.115 (1941); Vol. 4, p.9 (1925).

α-BROMO-*n*-CAPROIC ACID

[Caproic acid, α-bromo-]



Submitted by H. T. Clarke and E. R. Taylor.
Checked by C. S. Marvel and R. L. Shriner.

1. Procedure

Two hundred grams (1.72 moles) of freshly distilled dry *n*-caproic acid (Note 1) is placed in a 1-l. flask with 300 g. (96 cc., 1.88 moles) of bromine which has been dried by washing once with 200 cc. of concentrated sulfuric acid (Note 2). A 3-cc. portion of phosphorus trichloride is cautiously added and the flask connected to a reflux condenser (Note 3), the top of which is connected with a trap and absorption bottle containing water. The mixture is then heated in a water or oil bath to 65–70°, at which temperature the reaction commences and hydrogen bromide is given off smoothly. After five to six hours, the bromine has all reacted (Note 4). Towards the end of the reaction, the temperature is allowed to rise to about 100°. The contents of the flask are now distilled under diminished pressure (Note 5). The fraction boiling at 132–140°/15 mm. is collected and weighs 280–298 g. (83–89 per cent of the theoretical amount).

2. Notes

1. The *n*-caproic acid can be prepared by the general procedure described in Org. Syn. **11**, 78, Note 8.
2. The reagents must be dry or the yield will be lowered.
3. A flask fitted with a ground-glass connection to the reflux condenser will assist in reducing the amount of tar.
4. For larger runs, a longer time is required. A run of 2 kg. of caproic acid requires about fifteen hours.
5. It is best to distil the first low-boiling fractions with a water pump, since a considerable amount of hydrogen bromide is evolved. In order to obtain a light-colored product, the distillation should take place under as low pressure as possible. The α-bromo-*n*-caproic acid boils at 116–125°/8 mm. The product obtained is sufficiently pure for most purposes; upon redistillation, however, it comes over almost entirely between 128° and 131°/10 mm.

3. Discussion

α-Bromo-*n*-caproic acid can be prepared by heating *n*-caproic acid with bromine in a sealed tube to 140°[1] and with bromine and phosphorus;[2] and by the action of heat on α-bromo-α-butylmalonic acid.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 48

References and Notes

1. Hüfner, Z. Chem. 616 (1868); J. prakt. Chem. (2) **1**, 7 (1870).
2. Auwers and Benhardi, Ber. **24**, 2222 (1891); Fischer, Ber. **33**, 2381 (1900); Abderhalden, Froehlich and Fuchs, Z. physiol. Chem. **86**, 455 (1913).
3. Adams and Marvel, J. Am. Chem. Soc. **42**, 319 (1920); Marvel and du Vigneaud, Org. Syn. **11**,

22.

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

sulfuric acid (7664-93-9)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

PHOSPHORUS (7723-14-0)

Caproic acid, α-bromo-,
α-bromo-n-caproic acid (616-05-7)

phosphorus trichloride (7719-12-2)

Caproic acid,
n-caproic acid (142-62-1)

α-bromo-α-butylmalonic acid