



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.

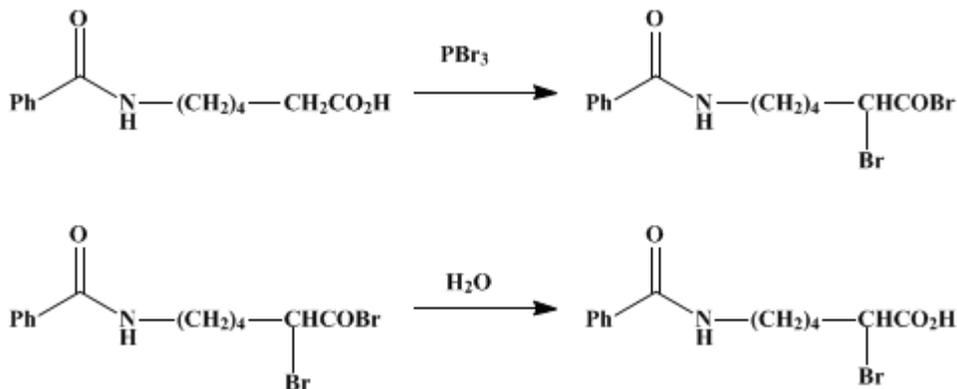
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.74 (1943); Vol. 19, p.18 (1939).

ϵ -BENZOYLAMINO- α -BROMOCAPROIC ACID

[Caproic acid, ϵ -benzamido- α -bromo-]



Submitted by J. C. Eck and C. S. Marvel.

Checked by C. R. Noller and William Munich.

1. Procedure

An intimate mixture of 150 g. (0.64 mole) of dry ϵ -benzoylaminocaproic acid (p. 76) and 26.4 g. (0.85 gram atom) of dry red phosphorus is placed in a 1-l. three-necked flask provided with a separatory funnel, an air-cooled condenser connected through a calcium chloride tube to a water trap, and a mechanical stirrer (Note 1). The reaction flask is surrounded by an ice-salt mixture, the stirrer started, and 408 g. (131 cc., 2.55 moles) of dry bromine added dropwise from the separatory funnel. When all the bromine has been added the cooling bath is removed. The mixture is warmed slowly at first and finally heated on a steam bath, with stirring, until the bromine vapors have practically disappeared. The hot mixture is poured slowly into 400 cc. of water in a 1-l. beaker with hand stirring. The viscous acid bromide reacts with the water with the evolution of heat, and the solid acid is formed. The lumps are pulverized, the mixture is replaced in the original reaction flask, and the whole is treated with a slow stream of sulfur dioxide to remove excess bromine. The solid product is filtered on a Büchner funnel, washed with three 50-cc. portions of water, and air-dried. The crude material is dissolved in 250 cc. of hot 95 per cent alcohol, filtered, and poured with stirring into 1 l. of cold water (Note 2). After filtering and air-drying, 130–180 g. (64–89 per cent of the calculated amount) of acid melting at 162–165° is obtained.

2. Notes

- The stirrer must be very powerful because the mixture becomes lumpy and finally very viscous. If the material agglomerates so badly that the stirrer will not operate, hand stirring may be necessary temporarily until the mass liquefies sufficiently to renew mechanical stirring. The checkers tried one run in which carbon tetrachloride was added to facilitate stirring, but, though it accomplished this purpose, the yield was only about half of that obtained without a liquid medium.
- The crude product may be recrystallized from ethyl alcohol, but the melting point is the same as that of the product obtained by precipitation with water, and the yield is considerably less.

3. Discussion

The above procedure¹ is essentially that of Braun.²

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2, 374*

References and Notes

1. Eck and Marvel, J. Biol. Chem. **106**, 387 (1934).
 2. Braun, Ber. **42**, 839 (1909).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

red phosphorus

ethyl alcohol,
alcohol (64-17-5)

bromine (7726-95-6)

sulfur dioxide (7446-09-5)

carbon tetrachloride (56-23-5)

ϵ -BENZOYLAMINO- α -BROMOCAPROIC ACID,
Caproic acid, ϵ -benzamido- α -bromo- (1700-05-6)

ϵ -Benzoylaminocaproic acid (956-09-2)