



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.

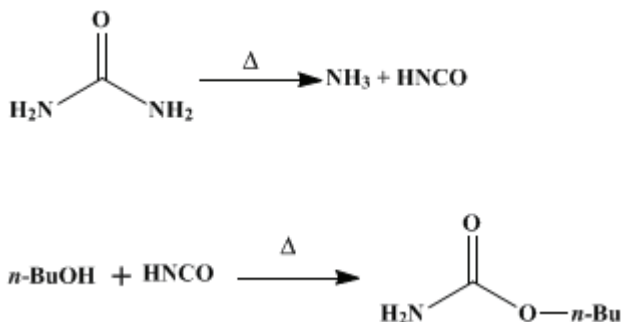
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

Organic Syntheses, Coll. Vol. 1, p.140 (1941); Vol. 9, p.24 (1929).

***n*-BUTYL CARBAMATE**

[Carbamic acid, butyl ester]



Submitted by Tenney L. Davis and Stanley C. Lane.
Checked by H. T. Clarke and L. G. S. Brooker.

1. Procedure

In a 2-l. round-bottomed flask fitted with a reflux condenser is placed 970 g. (1200 cc., 13.1 moles) of *n*-butyl alcohol. This is warmed, and 180 g. (3 moles) of urea is added to the warm liquid in small portions, with shaking. While the temperature rises, care must be taken that the urea goes into solution without melting and does not form a layer of molten urea beneath the solution (Note 1). The last portions of the urea are finally dissolved by boiling the liquid. The solution is then refluxed for thirty hours (Note 2), during which time ammonia escapes from the top of the condenser (Note 3). The reflux condenser is then removed and the liquid is distilled through an efficient column until the temperature of the liquid reaches 150°. The distillate consists of butyl alcohol containing ammonia and may be used directly in another run. The material which remains in the flask solidifies on cooling. It is boiled with 1 l. of ligroin (b.p. 60–90°) (Note 4), filtered, and the undissolved solid again boiled with two 100-cc. portions of ligroin, filtered, and finally washed on the filter with 100 cc. more of warm ligroin. The white gritty material which remains undissolved is practically pure cyanuric acid (Note 5). The yield of cyanuric acid is 12–18 g. (9–14 per cent of the theoretical amount).

The combined ligroin filtrates and washings are distilled under atmospheric pressure, using a column, until the temperature of the liquid reaches 150°. The residue is then distilled under reduced pressure and the fraction boiling at 108–109°/14 mm. (Note 6) is collected. The product is pure and melts at 53–54°. The yield is 263–266 g. (75–76 per cent of the theoretical amount).

2. Notes

1. If molten urea settles to the bottom near the source of heat, it will cause the liquid to bump and will decompose to produce cyanuric acid to the detriment of the yield of butyl carbamate.
2. If thirty hours of continuous heating is impracticable, care must be taken, on resuming the heating, that the urea goes into solution without melting.
3. A small amount of ammonium carbamate collects in the condenser during the reaction and may cause clogging. This should be removed from time to time by pushing it down by means of a glass tube which fits snugly into the condenser. The gases evolved when the solid falls into the hot liquid are carried off through the tube.
4. "Aviation" gasoline (86° Baumé) may also be employed if it is first distilled and the fraction boiling above 120° rejected.
5. The extraction with ligroin may be completed satisfactorily by means of the apparatus described on p. 375. Butyl allophanate is not soluble in ligroin and, if present, would remain with the cyanuric acid. However, when the material which is insoluble in ligroin is washed with hot acetone the washings yield no appreciable residue on evaporation. This is evidence that butyl allophanate and urea are not present

in the cyanuric acid.

6. *n*-Butyl carbamate boils under atmospheric pressure at 203–204° with some decomposition. The products of the decomposition are butyl alcohol and cyanuric acid.

3. Discussion

No reference to the preparation of *n*-butyl carbamate is to be found in the literature. The procedure described is adapted from that of Cahours,¹ who prepared *n*-propyl carbamate by heating propyl alcohol with urea. *n*-Butyl carbamate has also been prepared by one of the editors by the action of *n*-butyl chloroformate upon ammonia. The preparation of carbamates of the higher alcohols can be carried out by heating the carbamate of a volatile alcohol with a higher alcohol.²

References and Notes

1. Cahours, Compt. rend. **76**, 1387 (1873).
 2. I. G. Farbenind. A.-G., Ger. pat. 565,319 [C. A. **27**, 1014 (1933)].
-

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

ligroin

ammonia (7664-41-7)

butyl alcohol,
n-butyl alcohol (71-36-3)

acetone (67-64-1)

Carbamic acid, butyl ester,
butyl carbamate,
n-BUTYL CARBAMATE (592-35-8)

urea (57-13-6)

cyanuric acid (108-80-5)

ammonium carbamate (1111-78-0)

Butyl allophanate

propyl alcohol (71-23-8)

n-propyl carbamate (627-12-3)

n-butyl chloroformate (592-34-7)