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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n-BUTYL BORATE

$$3\ n\text{-BuOH} + B(OH)_3 \xrightarrow{\Delta} B(O\text{-}n\text{-Bu})_3$$

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1. Procedure

In a 2-l. round-bottomed flask, equipped with a 200-cc. dropping funnel and a 30-cm. column filled with glass beads (Note 1), and connected to a 40–50 cm. condenser, are placed 124 g. (2 moles) of boric acid, 666 g. (9 moles) of technical *n*-butyl alcohol, and a few chips of porous plate. The reaction mixture is heated to gentle boiling, and the rate of heating is adjusted so that 90–100 cc. of distillate is collected per hour. The temperature of the vapor at the top of the column remains constant at 91° over a period of three to three and one-half hours while the azeotropic mixture of *n*-butyl alcohol and water distils (Note 2). After two hours, the upper layer of *n*-butyl alcohol in the distillate is separated from the water, dried with a little anhydrous potassium carbonate or magnesium sulfate, and returned to the reaction mixture through the separatory funnel. Likewise, after the third hour of heating, the *n*-butyl alcohol in the distillate is separated, dried, and returned to the reaction flask.

During the third hour of heating, the temperature at the top of the column rises slowly as the removal of the water approaches completion. After the fourth hour, when the temperature of the distilling vapor has attained 110–112°, the heating is discontinued, and the reaction mixture is transferred to a 2-l. Claisen flask with the least possible exposure to atmospheric moisture (Note 3). The unreacted *n*-butyl alcohol is removed by distillation under reduced pressure (Note 4) until the thermometer registers a sudden rise in temperature. The receiver is then changed, and the main fraction of *n*-butyl borate distils almost entirely at 103–105°/8 mm. or 114–115°/15 mm. A negligible residue remains in the distilling flask. The weight of the distilled *n*-butyl borate, which contains a small amount of *n*-butyl alcohol, is 410–435 g. (89–94 per cent of the theoretical amount). From the aqueous distillate and the fore-run of the vacuum distillation, 190–210 g. of *n*-butyl alcohol is recovered.

The main fraction of *n*-butyl borate is redistilled from a Claisen flask provided with an indented fractionating column (Note 5), and the first 4–6 cc. of distillate is rejected. The purified product, b.p. 103–105°/8 mm. or 114–115°/15 mm., weighs 400–425 g. (87–92 per cent of the theoretical amount) (Note 6).

2. Notes

1. Any fractionating column of a reasonably effective type can be used. Columns longer than 30 cm. and of the most efficient types were found to give no better results than a simple Hempel column filled with glass beads or broken glass.
2. The distillate collected while the temperature remains at 91° separates into two layers; 100 cc. of this distillate contains 72 cc. of a supernatant layer of wet *n*-butyl alcohol.
3. Since *n*-butyl borate is hydrolyzed readily by atmospheric moisture, it is necessary to manipulate the reaction product so as to minimize exposure to the air.
4. *n*-Butyl borate can be purified by distillation at atmospheric pressure, but the separation from *n*-butyl alcohol is effected more readily under reduced pressure. *n*-Butyl borate is stated[1] to boil at 190°/200 mm. and at 230–235° under atmospheric pressure.
5. It is advantageous to use a Claisen flask with a 25–30 cm. side arm bearing a condenser jacket and connected to a device for collecting the fractions without interruption of the distillation or exposure to moist air.
6. *n*-Amyl borate can be prepared in a similar manner. From 792 g. (9 moles) of *n*-amyl alcohol and 124 g. (2 moles) of boric acid there is obtained 510–525 g. (93–96 per cent of the theoretical amount) of *n*-amyl borate, b.p. 146–148°/16 mm.; 210–215 g. of *n*-amyl alcohol is recovered. In this preparation the

temperature of the distilling vapor remains at 95° during the first two hours and the distillate contains relatively more water (100 cc. of distillate contains 56 cc. of water and 44 cc. of *n*-amyl alcohol). After the second hour the temperature rises slowly to 136–137°. It is unnecessary, and not advantageous, to return the recovered *n*-amyl alcohol to the reaction mixture.

3. Discussion

The procedure described is essentially that disclosed in a patent.[1] *n*-Butyl borate can also be prepared by the action of *n*-butyl alcohol on boron triacetate or boric anhydride.

References and Notes

1. W. J. Bannister, U. S. pat. 1,668,797 [C. A. **22**, 2172 (1928)].

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

potassium carbonate (584-08-7)

n-butyl alcohol (71-36-3)

boric acid (10043-35-3)

n-amyl alcohol (71-41-0)

magnesium sulfate (7487-88-9)

boron triacetate

boric anhydride

n-BUTYL BORATE (688-74-4)

n-Amyl borate (621-78-3)