



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.

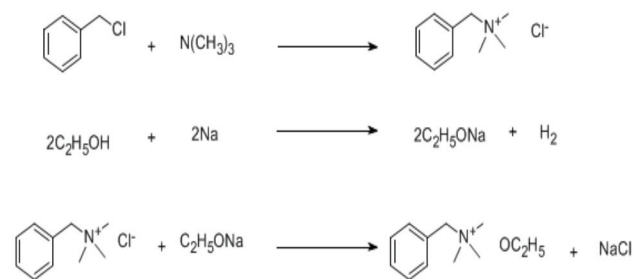
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 4, p.98 (1963); Vol. 38, p.5 (1958).

BENZYLTRIMETHYLAMMONIUM ETHOXIDE

[Ammonium, benzyltrimethyl-, ethoxide]



Submitted by W. J. Croxall, Marion F. Fegley, and H. J. Schneider¹.

Checked by John C. Sheehan and M. Gertrude Howell.

1. Procedure

A 3-l. three-necked flask (flask *A*) is fitted with a nitrogen inlet, a reflux condenser protected by a soda-lime tube, and a reflux condenser fitted with a dropping funnel protected by a soda-lime tube.

A second 3-l. three-necked flask (flask *B*) is fitted with a gas-tight modified Hershberg stirrer (Note 1), a gas inlet tube, and an appropriately designed gas outlet tube bearing a thermometer and connections leading to a soda-lime tube and an open-end mercury manometer. All rubber stoppers and connections are wired in place with 16-gauge copper wire.

Sodium (69 g., 3 g. atoms) is introduced into flask *A*, which had been flushed previously with nitrogen (Note 2). Ethanol (1.2 kg.) (Note 3) is added at such a rate that a continuous reflux is maintained. After the sodium is completely dissolved, the solution is allowed to cool to room temperature. During this period the benzyltrimethylammonium chloride is prepared.

A solution of 379.5 g. (3 moles) of benzyl chloride (Note 4) dissolved in 750 g. of anhydrous ethanol (Note 3) is placed in flask *B*. The system is flushed with trimethylamine previously dried by passage through a soda-lime tower. The gas outlet is closed and connected to the manometer. Over a period of 80 minutes, 195 g. (3.3 moles) of trimethylamine (Note 5) is introduced with stirring. The reaction is exothermic and must be cooled to keep the temperature below 50°. After the amine addition is complete, the solution is kept at 50° under an amine pressure of 5 cm. of mercury above atmospheric pressure for 1 hour. The mixture is then cooled to room temperature under an amine atmosphere.

The inlet tube of flask *B* is replaced by a rubber stopper bearing a short glass outlet tube and a glass inlet tube which is connected to an appropriately designed glass siphon outlet tube extending to the bottom of flask *A*. Gentle suction applied to the outlet tube of flask *B* draws the ethoxide solution slowly into flask *B*. The benzyltrimethylammonium chloride solution is stirred throughout the addition of the sodium ethoxide. After the transfer of the sodium ethoxide is completed, the finely divided precipitate of sodium chloride is allowed to settle overnight. When the sodium chloride has completely settled, the stopper bearing the inlet and outlet tubes is replaced by a stopper bearing a 15-in. length of 19-mm. glass tubing which is attached in turn by a gum rubber connection to a clean, dry, 1-gal. bottle fitted with an inlet tube and an outlet tube protected by soda-lime. The bottle is flushed with nitrogen before use. The 15-in. tube is adjusted so that the bottom is approximately ½ in. above the level of the precipitated sodium chloride. With the open-end manometer sealed off by a screw clamp, nitrogen pressure is applied through the outlet tube of the flask until 1.7–1.9 kg. of supernatant liquor is forced from the flask into the bottle (Note 6). This solution contains 24–30% benzyltrimethylammonium ethoxide (2.1–2.7 moles), as determined by titration with 0.1*N* hydrochloric acid, using methyl red as indicator. This represents a yield of 70–90%. An additional 270–400 g. of solution is obtained by filtration of the residual mixture under nitrogen. To ensure rapid filtration, a filter aid, such as Filtercel (Note 7), must be employed. The filtrate contains 24–30% benzyltrimethylammonium ethoxide (0.3–0.7 mole). The total yield is 89–100%. The solutions are stored under nitrogen and refrigeration in bottles sealed with rubber stoppers which are wired in place (Note 8).

Three hundred and thirty-five grams of the 25% ethanolic solution of benzyltrimethylammonium ethoxide (0.43 mole) is placed under nitrogen in a 3-l. three-necked flask equipped with a gas inlet tube, a gas-tight modified Hershberg stirrer (Note 1), and a gas outlet tube fitted with a thermometer. All stoppers and rubber connections are wired in place with 16-gauge copper wire. There is obtained by evaporation at 40° (Note 9) under reduced pressure (Note 10) 97 g. (0.40

mole) of the ethoxide containing an equivalent of [ethanol](#). The vacuum is broken with dry [nitrogen](#).

2. Notes

1. The stirrer is of the type designed by Hershberg,² but it has a single paddle of 16-gauge Nichrome wire.
2. A bubble counter is employed for indicating [nitrogen](#) flow.
3. The water content of the [ethanol](#), determined by Karl Fischer analysis, is 0.02–0.10%.
4. [Benzyl chloride](#) is redistilled before use. The fraction collected at 40–41° /6 mm. is used.
5. The flask is disconnected periodically from the gas train and stirring mechanism for weighing.
6. In small-scale preparations (approximately 0.5 mole) centrifugation of the total mixture is a convenient method for separation of the product from [sodium chloride](#).
7. Filtercel is supplied by Johns-Manville Corporation.
8. This method is more satisfactory than storage of the [benzyltrimethylammonium ethoxide monoethanolate](#). The excess [ethanol](#) is removed as necessary.
9. The temperature is maintained by surrounding the flask with a warm water bath. Higher temperatures are not recommended because of the tendency of the quaternary [ammonium ethoxide](#) to decompose.
10. The bulk of the [ethanol](#) was removed by using a water pump (40–50 mm.) and collected in 1-l. and 200-ml. Dry Ice traps connected in series. The remaining [ethanol](#) was removed by using an oil pump protected with two 300-ml. Dry Ice traps.

3. Discussion

The procedure described is adapted from the preparation outlined by Meisenheimer.³ The method has been applied by the authors to the preparation of [benzyltrimethylammonium methoxide](#), [dibenzyltrimethylammonium methoxide](#), [bis\(isopropyl\)benzyltrimethylammonium methoxide](#) and [benzyltriethylammonium ethoxide](#).

References and Notes

1. Rohm and Haas Company, Philadelphia 37, Pennsylvania.
 2. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).
 3. Meisenheimer and Bratring, *Ann.*, **397**, 295 (1913).
-

Appendix

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

Methyl Red

[ethanol](#) (64-17-5)

[hydrochloric acid](#) (7647-01-0)

[sodium chloride](#) (7647-14-5)

[nitrogen](#) (7727-37-9)

[mercury](#) (7439-97-6)

[sodium](#) (13966-32-0)

[sodium ethoxide](#) (141-52-6)

[benzyl chloride](#) (100-44-7)

[Trimethylamine](#) (75-50-3)

[Benzyltrimethylammonium ethoxide](#),
[Ammonium, benzyltrimethyl-, ethoxide](#) (27292-06-4)

[benzyltrimethylammonium chloride](#) (56-93-9)

[benzyltrimethylammonium ethoxide monoethanolate](#)
[ammonium ethoxide](#)

[benzyltriethylammonium ethoxide](#)

benzyltrimethylammonium methoxide (122-08-7)

dibenzyltrimethylammonium methoxide

bis(isopropyl)benzyltrimethylammonium methoxide

Copyright © 1921-2007, Organic Syntheses, Inc. All Rights Reserved