



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.

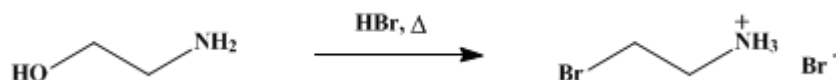
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.91 (1943); Vol. 18, p.13 (1938).

β-BROMOETHYLAMINE HYDROBROMIDE

[Ethylamine, 2-bromo-, hydrobromide]



Submitted by Frank Cortese

Checked by C. S. Marvel and C. L. Fleming.

1. Procedure

One kilogram (16.4 moles) of ice-cold [ethanolamine](#) ([Note 1](#)) is added, through a dropping funnel, with mechanical stirring, to 7 l. (9.94 kg., 52 moles) of ice-cold [hydrobromic acid](#) (sp. gr. 1.42) ([Note 2](#)) contained in a 12-l. round-bottomed flask. The flask is attached to an efficient fractionating column and heated until 1850 cc. of distillate has been collected. The rate of heating is then diminished to a point at which the liquid ceases to distil and merely refluxes. The heating under reflux is continued for one hour. At the end of this time, 700 cc. more is distilled, and the solution is again heated under reflux for one hour. This procedure is followed with 600-, 300-, 250-, 150-, 100-, and 50-cc. portions of distillate. The process may be interrupted at any time. The solution is finally heated under reflux for three hours, and 2.3 l. of crude [hydrobromic acid](#) distilled. The total volume of distillate, including that which is collected during refluxing, must not be less than 6270 cc. or more than 6330 cc.

The dark-colored residue is divided into two approximately equal portions, and each is poured, while still hot, into a 4-l. beaker. After the liquid has cooled to about 70°, 1650 cc. of [acetone](#) is added to each portion. The mixture is stirred well, so that as much as possible of the dark-colored solid is brought into contact with the [acetone](#). After standing in the icebox overnight, the [β-bromoethylamine hydrobromide](#) is collected on a filter, washed with [acetone](#) until colorless ([Note 3](#)), and air-dried for about fifteen minutes. The filtrates are combined, concentrated to a volume of 1 l., and cooled. After seeding, a second crop of nearly pure material is obtained. By evaporation to a syrup, cooling, and seeding, a third crop of slightly colored material is obtained. ([Note 4](#)). The yield is about 2.8 kg. (83 per cent of the theoretical amount) ([Note 5](#)).

2. Notes

1. Commercial [ethanolamine](#) is fractionated in a glass apparatus, and the fraction boiling at 167–169° is used.
2. The [hydrobromic acid](#) must have a specific gravity of at least 1.42.
3. It may be advisable for effective washing to transfer the crude cake to a mortar and crush it.
4. All three crops are suitable for use in the synthesis of [taurine](#) described on [p. 564](#).
5. The procedure has been applied to the preparation of the following β-dialkylaminoethyl [bromide hydrobromides](#).

R	Yield, Per Cent	Heating Periods
CH ₃	83	1–1.5 hr., 2 hr.
C ₂ H ₅	80	1 hr., 2 hr.
<i>n</i> -C ₃ H ₇	55	0.75 hr., 2 hr.
<i>n</i> -C ₄ H ₉	20	1 hr., 3 hr.
<i>n</i> -C ₄ H ₉	59	0.5 hr., 2 hr.

The final distillation was not always carried as far as called for by the procedure of Cortese. If a faint brown or violet color appeared in the distillate, or if white fumes were given off, the distillation was discontinued; further distillation seemed to cause decomposition. However, the color always came near the end point specified in the procedure above and the total volume of the distillates was never less than 95 per cent of that called for. Since the solubilities of the products in [acetone](#) range from very slight to extreme as the molecular weights increase, the extraction of the products requires variations in the amounts of [acetone](#) specified above. [Lawrence H. Amundsen and Karl W. Krantz, private communication, and J. Am. Chem. Soc. **63**, 305 (1941).]

3. Discussion

[β-Bromoethylamine hydrobromide](#) has been prepared by the reaction of [potassium phthalimide](#) with [ethylene bromide](#), followed by hydrolysis;¹ by the addition of [hydrogen bromide](#) to [ethyleneimine](#);² from [ethanolamine](#) and [hydrobromic acid](#);³ and from [ethanolamine](#) and [hydrogen bromide](#) at 140–190°.⁴ The preparation from [ethyleneimine](#) and [hydrogen bromide](#) is reported to succeed only if the imine is added to the acid.⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 563](#)
- [Org. Syn. Coll. Vol. 3, 254](#)
- [Org. Syn. Coll. Vol. 4, 333](#)

References and Notes

1. Gabriel, Ber. **21**, 566 (1888).
 2. Gabriel, *ibid.* **21**, 1054 (1888); Gabriel and Stelzner, *ibid.* **28**, 2929 (1895).
 3. Gabriel, *ibid.* **50**, 826 (1917); Cortese, J. Am. Chem. Soc. **58**, 191 (1936).
 4. I. G. Farbenind. A.-G., Brit. pat. 468,387 [C. A. **31**, 8545 (1937)].
 5. Masters and Bogert, J. Am. Chem. Soc. **64**, 2710 (1942).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[bromide](#) (24959-67-9)

[HYDROBROMIC ACID](#),
[hydrogen bromide](#) (10035-10-6)

[acetone](#) (67-64-1)

[Potassium Phthalimide](#) (1074-82-4)

[ethylene bromide](#) (106-93-4)

[β-Bromoethylamine hydrobromide](#),
[Ethylamine, 2-bromo-, hydrobromide](#) (2576-47-8)

[ethanolamine](#) (141-43-5)

Taurine (107-35-7)

ethyleneimine (9002-98-6)

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