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.

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.

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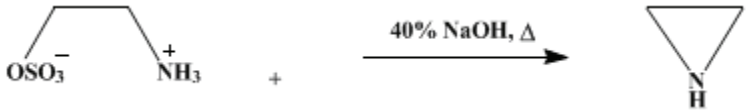
ETHYLENIMINE



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1. Procedure

Caution! This preparation should be carried out in a good hood, and it is advisable to use rubber gloves.

In a 5-l. flask surmounted by a water-cooled still head connected to a 30-in. spiral condenser set for downward distillation and connected to a well-cooled receiver (Note 1), 564 g. (4 moles) of β-aminoethylsulfuric acid (Note 2) is mixed with 1760 g. (1230 ml.) of 40% sodium hydroxide solution (704 g. of sodium hydroxide in 1056 ml. of water). The mixture is heated with a free flame until it just begins to boil. At this point external heating is discontinued (Note 3). The reaction that begins at the boiling point keeps the mixture boiling for several minutes. When this initial reaction has subsided, heating is resumed and about 500 ml. of distillate is collected as quickly as possible in the well-cooled receiver. To the chilled distillate 450–500 g. of potassium hydroxide pellets is added gradually, whereupon the imine separates as an upper layer. The organic layers from four such 4-mole runs are combined and left overnight in a refrigerator over about 400 g. of potassium hydroxide pellets. The aqueous layers are combined and distilled through a wrapped 10-in. Vigreux column attached to a 30-in. spiral condenser. The distillate boiling at 50–100° is chilled thoroughly, and 200–250 g. of potassium hydroxide pellets is added gradually. The upper layer of crude ethylenimine is separated and combined with the larger portion of base (Note 4) and (Note 5).

If an aqueous layer appears during drying of the combined organic layers, the upper layer (about 575–600 g.) is again separated, 200 g. of potassium hydroxide pellets is added, and the whole is distilled through the same apparatus as that used for distilling the aqueous portion. If no layer appears, the base is decanted from the hydroxide and distilled from a fresh 200-g. portion of potassium hydroxide. The fraction boiling at 50–100° (about 350 g.) is collected and dried over 100 g. of potassium hydroxide pellets.

The crude ethylenimine is separated and dried over fresh 100-g. portions of potassium hydroxide until an aqueous layer no longer appears (Note 6). It is then decanted from the drying agent and redistilled from 100 g. of potassium hydroxide.

The yield of ethylenimine (b.p. 56–58°) is 235–250 g. (34–37%). A stick of sodium hydroxide is added to act as a preservative, and the material is best stored in sealed bottles in a refrigerator (Note 7), (Note 8), and (Note 9).

2. Notes

1. Cooling the receiver in a freezing mixture will cut the loss of the distillate to a minimum.
2. β-Aminoethylsulfuric acid of excellent quality is available from the B. F. Goodrich Company.
3. It is well to have an ice bath available to control the exothermic reaction, which may become quite violent.
4. The use of an efficient distilling column is recommended because the crude base contains higher-boiling by-products. One of these is the dimer, N-β-aminoethylethylenimine; b.p. 126–127.5°.
5. It has been suggested that the portion of ethylenimine, boiling at 50–100°, might be collected directly on distillation without separating the organic layer from the aqueous potassium hydroxide layer. This is not advisable, because heating ethylenimine in the presence of a base appears to increase

polymerization. The quantity of the organic base contained in the concentrated aqueous solution of potassium hydroxide is sufficient, however, to warrant this distillation of the aqueous layer.
6. If the original separation is done carefully and if sufficient potassium hydroxide is used, an aqueous layer will separate during the first drying only. Should this not be the case, it may be worth while to combine all aqueous portions obtained and redistil them to obtain any material boiling at 50–100°.
7. Yields of 26.5% and 32% of ethylenimine have been reported.[2,3]
8. Ethylenimine is strongly caustic and burns the skin. Inhalation of the vapor causes acute inflammation of the eyes, nose, and throat, with symptoms resembling those of bronchitis. After two or three days, the irritation subsides and the tissues return to normal, without suffering any apparent permanent injury. Continued exposure to the vapor may cause an individual to acquire an extreme sensitivity to it. Ethylenimine is also very inflammable and polymerizes with explosive violence under certain conditions.[4,5]
9. Redistillation over fresh potassium hydroxide of the residue from this final distillation gives an additional 10–15 g. of ethylenimine, boiling at 56–58°. This redistillation is advisable when the residues from three to four 16-mole batches are combined.

3. Discussion

Ethylenimine has been prepared from β-bromoethylamine hydrobromide by reaction with silver oxide,[6] potassium hydroxide,[7] or sodium methoxide;[8] from β-chloroethylamine hydrochloride by reaction with sodium methoxide[8] or sodium hydroxide;[9] from β-aminoethylsulfuric acid by reaction with sodium hydroxide;[2,3,4,10,11] and by heating oxazolidone, or substances yielding it, to 100–300°.[12]

References and Notes

1. Eastman Kodak Company, Rochester, New York.
2. Wenker, *J. Am. Chem. Soc.*, **57**, 2328 (1935); Leighton, Perkins, and Renquist, *J. Am. Chem. Soc.*, **69**, 1540 (1947).
3. Jones, Langsjoen, Neumann, and Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).
4. Mills and Bogert, *J. Am. Chem. Soc.*, **62**, 1177 (1940).
5. Pingree, *Am. Dyestuff Reptr.*, **35**, 124 (1946).
6. Gabriel, *Ber.*, **21**, 1049 (1888).
7. Gabriel, *Ber.*, **21**, 2665 (1888); Gabriel and Stelzner, *Ber.*, **28**, 2929 (1895).
8. Knorr and Meyer, *Ber.*, **38**, 3130 (1905).
9. U. S. pat. 2,212,146 [*C. A.*, **35**, 463 (1941)].
10. Brit. pat. 460,888 [*C. A.*, **31**, 4676 (1937)].
11. Reeves, Drake, and Hoffpauir, *J. Am. Chem. Soc.*, **73**, 3522 (1951).
12. Sundén (to Stockholms Superfosfat Fabriks A/B), Swed. pat. 148,559 [*C. A.*, **50**, 2679 (1956)].

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

sodium hydroxide (1310-73-2)

silver oxide (20667-12-3)

sodium methoxide (124-41-4)

potassium hydroxide (1310-58-3)

β-Bromoethylamine hydrobromide (2576-47-8)

Ethylenimine (9002-98-6)

β-aminoethylsulfuric acid (926-39-6)

N-β-aminoethylethylenimine

β-chloroethylamine hydrochloride (870-24-6)

oxazolidone (497-25-6)