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.

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.

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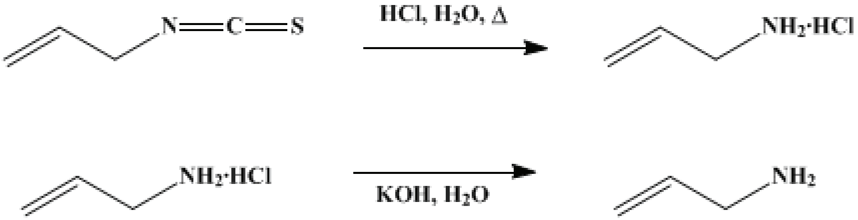
ALLYLAMINE



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1. Procedure

In a 5-l. round-bottomed flask, equipped with a reflux condenser connected to a gas trap (Note 1), are placed 2 l. (12.1 moles) of 20 per cent hydrochloric acid and 500 g. (5.05 moles) of allyl isothiocyanate (Note 2). The mixture is refluxed over a free flame until the upper layer of allyl isothiocyanate has completely disappeared, about fifteen hours being required for the hydrolysis. When the reaction is complete, the solution is poured into a 3-l. beaker and concentrated on the steam bath until crystals begin to form in the hot solution. This occurs when the volume is approximately 400 cc. (Note 3).

The warm residue is then diluted with water to a volume of 500–550 cc. and placed in a 2-l. three-necked, round-bottomed flask equipped with a 500-cc. dropping funnel, a mercury-sealed mechanical stirrer, and a condenser arranged for distillation. The lower end of the condenser is fitted to a receiver consisting of a 500-cc. suction flask, whose side arm is connected to a reflux condenser (Note 4). The receiver is placed in an ice-salt bath and the three-necked flask in a water bath. The temperature of the water bath is raised to 95–98°, the stirrer is started, and a solution of 400 g. (7.1 moles) of potassium hydroxide in 250 cc. of water is added dropwise from the funnel. As soon as the free hydrochloric acid is neutralized, the amine begins to distil. The rate of the addition of the alkali is regulated so as to maintain a dropwise distillation of allylamine and, after the addition is complete, heating and stirring are continued until all the amine has distilled.

The distillate is then dried over solid potassium hydroxide for twenty-four hours and finally over metallic sodium (Note 5). The allylamine is distilled from a water bath held at 70–78°, through a 12-in. fractionating column, into a receiver immersed in an ice bath. Two fractions are collected: up to 54°/746 mm., and 54–57°/746 mm. The lower fraction amounts to 14–16 g. and on redistillation yields 6–8 g. of pure material. The total yield of pure allylamine boiling at 54–57°/746 mm. is 200–210 g. (70–73 per cent of the theoretical amount).

2. Notes

1. It is desirable to use a gas trap in order to prevent vapors of allyl isothiocyanate from escaping into the room. The gas trap described on p. 4 is suitable.
2. Eastman's "practical" grade (b.p. 150–152°) of allyl isothiocyanate was used in this preparation.
3. The rate of evaporation is greatly accelerated by allowing a stream of air to blow across the surface of the hot liquid. It is advantageous for the evaporation to proceed as far as possible in order to remove most of the free hydrochloric acid, and no harm is done if it continues until the solution turns to a semi-solid mass of crystals.
4. Care must be taken throughout to prevent loss of the product by volatilization. Furthermore, the vapors should not be allowed to come into contact with the nasal passages, as violent sneezing is produced.
5. The distillate should be kept cold (5–10°) during the drying process and should be separated from the potassium hydroxide before drying with sodium.

3. Discussion

Allylamine has been prepared by the hydrolysis of allyl isothiocyanate with dilute sulfuric[1] or hydrochloric[2] acid.

References and Notes

1. Hofmann, Ber. **1**, 183 (1868).
2. Gabriel and Eschenbach, ibid. **30**, 1124 (1897).

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

hydrochloric acid (7647-01-0)

potassium hydroxide (1310-58-3)

sodium,
metallic sodium (13966-32-0)

Allylamine (107-11-9)

allyl isothiocyanate (57-06-7)