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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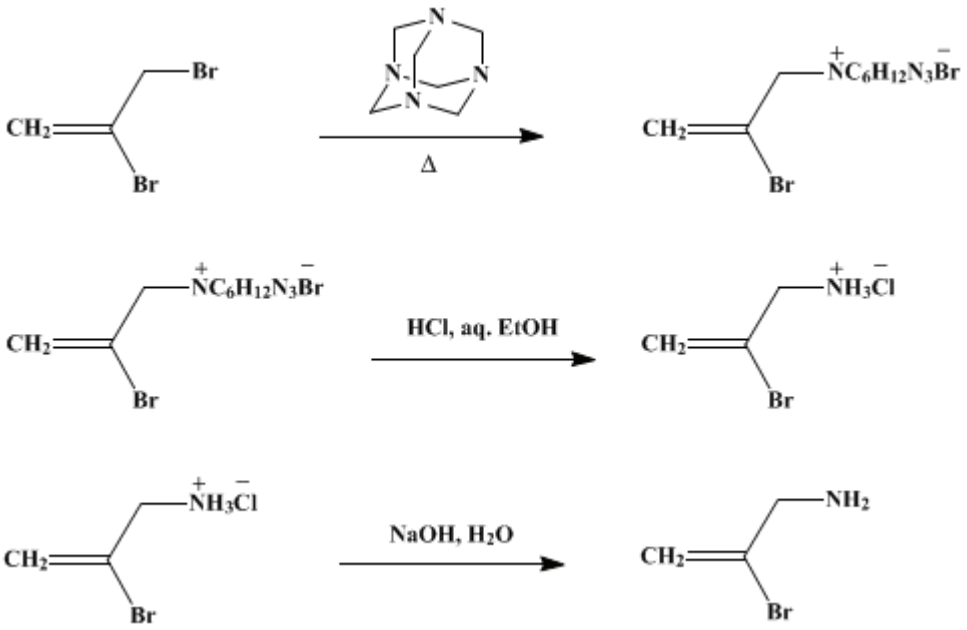
2-BROMOALLYLAMINE

[Allylamine, 2-bromo-]



Submitted by Albert T. Bottini, Vasu Dev, and Jane Klinck[1].
Checked by A. S. Pagano and W. D. Emmons.

1. Procedure

Caution! Contact with 2-bromoallylamine can cause severe eye and skin irritation. This preparation should be carried out in a good hood, and the operator should wear protective goggles and rubber gloves.

A. *2-Bromoallylhexaminium bromide*. A 2-l. three-necked flask fitted with a Hershberg stirrer,[2] a dropping funnel, and a condenser is charged with a solution of 154 g. (1.10 moles) of hexamethylenetetramine (Note 1) in 1250 ml. of chloroform. The solution is stirred and heated under reflux while 200 g. (1.00 mole) of 2,3-dibromopropene (Note 2) is added dropwise over a period of 1 hour. Precipitation of the product is noted soon after the first addition of 2,3-dibromopropene. After the addition is complete, the reaction mixture is stirred under reflux for 3 hours and allowed to stand overnight. The mixture is cooled in an ice bath, and the salt is collected by suction filtration. After air-drying, the crude yellow 2-bromoallylhexaminium bromide weighs 292–308 g. (86–91%) and melts at 183–186°.

B. *2-Bromoallylamine*. Crude 2-bromoallylhexaminium bromide (204 g., 0.60 mole) is dissolved in a warm solution prepared from 400 ml. of water, 2 l. of ethanol, and 480 ml. (5.8 moles) of 12*N* hydrochloric acid. A white precipitate of ammonium chloride forms within an hour. The reaction mixture is allowed to stand for 24 hours, and the precipitate is removed by suction filtration. The mother liquor is concentrated to a volume of 600 ml. (Note 3), and the precipitate (Note 4) is removed by suction filtration. The mother liquor is evaporated to dryness (Note 5), and the residue is dissolved in 300 ml. of water. The solution is cooled in an ice bath and made strongly alkaline (pH 13) with 6*N* sodium hydroxide solution.

The two-phase mixture is placed in a separatory funnel, and the heavy red-brown oil is separated. The aqueous phase is extracted with 100 ml. of ether. The oil and the ether extract are combined,

washed with 50 ml. of saturated sodium chloride, and dried over potassium carbonate. The drying agent is removed by filtration, and the filtrate is distilled. Colorless 2-bromoallylamine is collected at 65–68°/100 mm.; weight 49–59 g. (59–72%); n_D^{25} 1.5075–1.5085 (Note 6).

2. Notes

1. The submitters used hexamethylenetetramine obtained from Matheson, Coleman and Bell.
2. The 2,3-dibromopropene was obtained from Columbia Organic Chemicals Co., Columbia, South Carolina, and was redistilled before use. The preparation of 2,3-dibromopropene is described in an earlier volume of this series.[3]
3. The submitters divided the mother liquor into 6 equal portions and concentrated each to a volume of 100 ml. at a pressure of 25 mm. in a 1-l. round-bottomed flask on a rotary film evaporator. The rotary film evaporator used was obtained from Cenco Scientific Co., Santa Clara, California.
4. The precipitate is ammonium chloride that contains virtually no 2-bromoallylamine hydrochloride.
5. The submitters used a rotary film evaporator to evaporate the mother liquor at a pressure of 25 mm. in a water bath heated to 90°.
6. 2-Bromoallylamine discolors slowly even when stored at 0° in a dark container. The refractometer to be used for determination of the refractive index should be placed in a good hood.

3. Discussion

2-Bromoallylamine has been prepared by heating N-(2-bromoallyl)-phthalimide with hydrazine in methanol;[4] by treatment of 2,3-dibromopropylamine hydrochloride with excess alcoholic potassium hydroxide;[5] by treatment of 1,2,3-tribromopropane with alcoholic ammonia at 100°;[6] and by the present procedure.[7]

4. Merits of the Preparation

This method gives better yields than other methods of preparation of 2-bromoallylamine, and it is the most convenient method for the preparation of large quantities of the compound. The procedure illustrates a reaction, the so-called Delépine reaction, that has been used for the preparation of many primary aliphatic amines.[8,9,10,11,12,13] It is especially useful in the preparation of derivatives of phenacylamine.[14,15,16] A number of primary aliphatic amines have been prepared by this method without isolation of the intermediate hexaminium salt.[11] Several preparations of aliphatic aldehydes via the hexaminium salt have been described in earlier volumes of this series.[17]

References and Notes

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

2-Bromoallylhexaminium bromide

ethanol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium chloride (7647-14-5)

potassium hydroxide (1310-58-3)

2,3-Dibromopropene (513-31-5)

1,2,3-Tribromopropane (96-11-7)

hydrazine (302-01-2)

hexamethylenetetramine (100-97-0)

2-Bromoallylamine,
Allylamine, 2-bromo- (6943-51-7)

2-bromoallylamine hydrochloride

N-(2-bromoallyl)-phthalimide

2,3-dibromopropylamine hydrochloride

phenacylamine