



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.

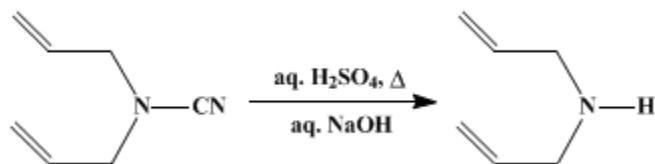
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.201 (1941); Vol. 5, p.43 (1925).

DIALLYLAMINE



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1. Procedure

A solution of 123 g. (67 cc., 1.2 moles) of **sulfuric acid** (sp. gr. 1.84) in 370 cc. of water is placed in a 2-l. round-bottomed flask equipped with a reflux condenser. To this is added 98.5 g. (0.81 mole) of **diallylcyanamide** (p. 203) and a few pieces of clay plate to prevent bumping. The mixture is refluxed gently for six hours. During the first fifteen minutes of heating, some bumping occurs. However, the mixture gradually becomes homogeneous and the boiling then proceeds smoothly (Note 1).

After six hours, the solution is cooled to room temperature and a cold solution of 192 g. (4.8 moles) of **sodium hydroxide** in 350 cc. of water is poured down the side of the flask so that most of it settles to the bottom without mixing with the solution in the flask. The flask is then connected to a condenser for downward distillation and is shaken to mix the two layers. The resulting free amine separates. The flask is heated and the amine, together with some water, distils. The distillation is continued until no amine separates from a test portion of the distillate. There is a small quantity of an oily liquid left floating in the flask. This is probably an impurity from the **diallylcyanamide**.

The weight of water in the distillate is estimated, and about one-half of this amount of **potassium hydroxide** is added in the form of sticks, so that it will dissolve slowly. The mixture should be kept cool while the **potassium hydroxide** is dissolving. Bubbles of **ammonia** gas will be evolved. When solution of the **potassium hydroxide** is complete, the amine is separated and dried for several hours over solid **sodium hydroxide** which has been freshly broken up into small lumps. It is then filtered into a distilling flask and distilled at atmospheric pressure. If the product has been thoroughly dried, there should be no low-boiling material. All the **diallylamine** should come over at 108–111° and only a very small amount of higher-boiling material should remain. The yield is 62–68 g. (80–88 per cent of the theoretical amount) (Note 2).

2. Notes

1. Alkali may be used for this hydrolysis instead of acid; but it is not so satisfactory, since the reaction mixture remains in two layers, thus causing the hydrolysis to proceed more slowly. Furthermore, any slight leak in the apparatus during refluxing permits a loss of product.

2. This reaction represents a general method for the preparation of secondary amines; thus, **di-n-butylamine** has been obtained from **di-n-butylcyanamide** in yields of 75 per cent of the theoretical amount.

3. Discussion

Diallylamine can be prepared from **allylamine** with **allyl bromide**¹ or with **allyl chloride**.² Experiments on these methods showed that the resulting product contained relatively large amounts of mono- and triallylamine, and it was very difficult to isolate pure **diallylamine**. The procedure described from **diallylcyanamide**³ is more satisfactory.

This preparation is referenced from:

References and Notes

1. Ladenburg, Ber. **14**, 1879 (1881).
 2. Liebermann and Hagen, Ber. **16**, 1641 (1883).
 3. Vliet, J. Am. Chem. Soc. **46**, 1307 (1924); "Versuche mit Diallylderivaten," Thesis by Paul Graf, Eidgen. Techn. Hochsch., Zürich, p. 29 (1922).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

mono- and triallylamine

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

Allyl bromide (106-95-6)

allyl chloride (107-05-1)

potassium hydroxide (1310-58-3)

Diallylamine (124-02-7)

Diallylcyanamide (538-08-9)

Allylamine (107-11-9)

di-n-butylamine (111-92-2)

di-n-butylcyanamide (2050-54-6)