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.

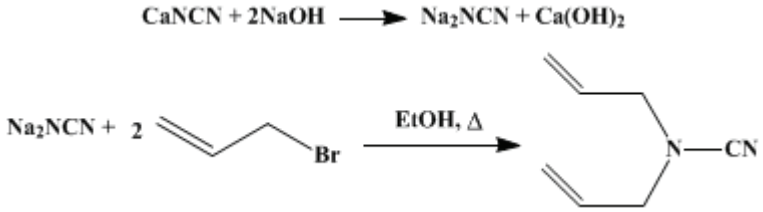
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

DOI:10.15227/orgsyn.005.0045

*Organic Syntheses, Coll. Vol. 1, p.203 (1941); Vol. 5, p.45 (1925).*

# DIALLYLCYANAMIDE

## [Cyanamide, diallyl-]




Submitted by E. B. Vliet
Checked by Roger Adams and E. E. Dreger.

## 1. Procedure

In a 5-l. round-bottomed, two-necked flask, fitted with a reflux condenser and a mechanical stirrer with a mercury seal, are placed 660 cc. of cold water and 135 g. of cracked ice. Two hundred grams (containing about 1.4 moles of pure calcium cyanamide) of fresh lime-nitrogen (Note 1) is added slowly, with stirring. As soon as the lime-nitrogen is suspended thoroughly in the water, a cold solution of 110 g. (2.75 moles) of sodium hydroxide in 200 cc. of water is added slowly, with stirring. Then the suspension is stirred quite briskly during one hour. If the temperature rises above 25°, small amounts of ice should be added (Note 2).

To the solution of sodium cyanamide thus prepared, 380 g. (3.14 moles) of allyl bromide (Note 3) and 660 cc. of 95 per cent alcohol are added. The mixture is then heated on a water bath with good stirring until it refluxes gently, and the heating and stirring are continued for two and one-half hours. Then the reflux condenser is replaced by one set downward for distillation. The stirring is continued and the alcohol is distilled until about 500 cc. has been collected. The distillate may be discarded or used for the recovery of alcohol (Note 4).

The reaction mixture is cooled to room temperature and filtered with suction through a large Büchner funnel. The residue is washed with alcohol. The filtrate which will be in two layers, is extracted twice with benzene, first with 270 cc. and then with 130 cc. The combined benzene extracts are dried with sodium sulfate and then filtered into a distilling flask. The benzene is distilled from a water bath, and then the diallylcyanamide is distilled under reduced pressure. It boils at 105–110°/18 mm.; at 128–133°/57 mm.; and at 140–145°/90 mm. There is a small residue of higher-boiling material. The yield of diallylcyanamide, boiling over a 5° range, is 90–97 g. (52–56 per cent of the theoretical amount based on the calcium cyanamide) (Note 5).

## 2. Notes

1. The lime-nitrogen used in this preparation should be the crude untreated product sold as fertilizer under the name "Cyanamid." It contains approximately 55 per cent calcium cyanamide, 20 per cent calcium oxide, 12 per cent graphite, and small amounts of various impurities. Lime-nitrogen should be protected from moisture when stored, in order to prevent slow polymerization to dicyanodiamide. It is advisable to use a fresh supply of lime-nitrogen for this synthesis.
2. Stirring for one hour in the cold permits the relatively insoluble calcium cyanamide to react with sodium hydroxide and go into solution as sodium cyanamide. If the temperature is not kept below 25° during this time, there is some tendency for polymerization to dicyanodiamide.
3. A good grade of allyl bromide should be used. A method for the preparation of allyl bromide is described on p. 27.
4. No allyl bromide is recovered. When water is added to the alcohol distillate, which would undoubtedly contain any unused allyl bromide, none separates. The excess probably reacts to form allyl alcohol. However, no attempt has been made to isolate it.

5. This represents a general procedure for the preparation of dialkylcyanamides; for example, di-*n*-butylcyanamide has been prepared in a similar manner, in yields of about 50 per cent of the theoretical amount.

## 3. Discussion

Diallylcyanamide can be prepared by the action of allyl bromide on disodium cyanamide.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 201

---

## References and Notes


1. Vliet, J. Am. Chem. Soc. **46**, 1307 (1924); U. S. pat. 1,659,793 [C. A. **22**, 1365 (1928)].


---

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

calcium cyanamide

sodium cyanamide

graphite

dicyanodiamide

disodium cyanamide

alcohol (64-17-5)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

Allyl bromide (106-95-6)

Allyl alcohol (107-18-6)

sodium sulfate (7757-82-6)

Diallylcyanamide,
Cyanamide, diallyl- (538-08-9)

calcium oxide

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