



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](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.

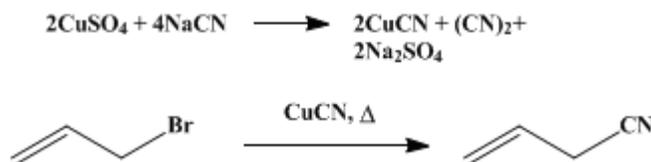
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.*

*Organic Syntheses, Coll. Vol. 1, p.46 (1941); Vol. 8, p.4 (1928).*

## ALLYL CYANIDE

### [3-Butenenitrile]



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### 1. Procedure

(A) *Preparation of Cuprous Cyanide.*—(Note 1)—In a 6-l. round-bottomed flask fitted with a stopper carrying a mechanical stirrer, a separatory funnel, and a gas exit tube leading to a good hood (Note 2), is placed a solution of 650 g. (2.6 moles) of crystallized copper sulfate in 4 l. of water. The flask is surrounded by an oil bath and heated to about 80°. The stirrer is started and a solution of 255 g. (5.2 moles) of sodium cyanide (Note 3) in 650 cc. of water is added from the separatory funnel over a period of about one-half hour. Then the mixture is boiled until no more cyanogen gas is evolved. This requires about five to ten minutes.

The cuprous cyanide, which begins to separate as a light tan precipitate as soon as any of the cyanide solution is added, is allowed to settle and the solution is decanted. The precipitate is filtered, then washed with water (1 l.) and finally with alcohol (500 cc.) and ether (300 cc.). After drying at 110° for about thirty-six hours, the product weighs 200–210 g. (85–90 per cent of the theoretical amount).

(B) *Allyl Cyanide.*—In a 1-l. round-bottomed flask fitted with a condenser (Note 4) and a mechanical stirrer are placed 220 g. (1.83 moles) of allyl bromide (Note 5) and 170 g. (1.9 moles) of dry cuprous cyanide (Note 6). The mixture is heated in a water bath and the stirrer rotated slowly by hand until the reaction starts (about fifteen to thirty minutes). When the reaction once begins, it becomes vigorous, and the heating bath must be replaced by a cooling mixture of ice and water in order to avoid loss of product through the condenser. After the vigorous reaction has subsided, the water bath is replaced, the mechanical stirrer is started and the mixture is heated until no more allyl bromide refluxes. This requires about one hour.

The condenser is then set for distillation and the allyl cyanide is distilled from the flask by heating it in an oil bath with stirring (Note 7) and (Note 8). Upon redistillation, the allyl cyanide is pure and boils at 116–121° with almost no loss. The yield is 98–103 g. (80–84 per cent of the theoretical amount).

### 2. Notes

1. Technical cuprous cyanide dried at 110° gives as good results as the specially prepared substance.
2. The cyanogen evolved in this reaction should be led into a flue with good suction draft or removed by a gas absorption trap (Fig. 7 on p. 97). It may be burned if a trap is placed in the system to allow the moisture to condense.
3. The ordinary technical sodium cyanide is used.
4. A very efficient condenser is needed as the mixture refluxes vigorously during the first part of the reaction. A condenser of the bulb type about 90 cm. long is satisfactory. If a less efficient condenser is used, the upper end should be fitted with a tube leading into an empty flask to catch any material forced out.
5. The allyl bromide (p. 27) should be dried over calcium chloride, filtered and redistilled, the fraction boiling at 69–71° being used.
6. The cuprous cyanide must be dry, as small amounts of moisture reduce the yield considerably (about

15 per cent). With some samples of technical [cuprous cyanide](#) a larger amount must be used.

7. Toward the end of this distillation it is advisable to connect with the suction to remove the last of the [allyl cyanide](#) from the solid residue in the flask.

8. The residue in the flask is very tarry. It is best removed by careful treatment with strong [nitric acid](#), then with water, and finally with hot [alcohol](#). If necessary, the treatment is repeated several times.

### 3. Discussion

[Allyl cyanide](#) can be prepared from [potassium cyanide](#) and [allyl chloride](#),<sup>1</sup> [allyl bromide](#)<sup>2</sup> and [allyl iodide](#).<sup>3</sup> The procedure described is essentially that of Bruylants,<sup>4</sup> who has shown that the yields are much better when dry [cuprous cyanide](#) is treated with [allyl bromide](#). [Allyl cyanide](#) can also be prepared from [allyl chloride](#) and [cuprous cyanide](#) or from [allyl alcohol](#), [cuprous cyanide](#) and [hydrochloric acid](#).<sup>5</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 851](#)

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### References and Notes

1. Pinner, Ber. **12**, 2053 (1879).
2. Pomeranz, Ann. **351**, 357 (1907); Lespieau, Compt. rend. **137**, 262 (1903); Bull. soc. chim. (3) **33**, 58 (1905).
3. Rinne and Tollens, Ann. **159**, 106 (1871).
4. Bruylants, Bull. soc. chim. Belg. **31**, 175 (1922).
5. Breckpot. ibid. **39**, 465 (1930); Glattfield and Rietz, J. Am. Chem. Soc. **62**, 974 (1940).

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### Appendix

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

[alcohol](#) (64-17-5)

[calcium chloride](#) (10043-52-4)

[hydrochloric acid](#) (7647-01-0)

[ether](#) (60-29-7)

[nitric acid](#) (7697-37-2)

[sodium cyanide](#) (143-33-9)

[Allyl bromide](#) (106-95-6)

[Allyl alcohol](#) (107-18-6)

[Allyl cyanide](#),  
[3-Butenenitrile](#) (109-75-1)

[Cuprous Cyanide](#) (544-92-3)

copper sulfate (7758-98-7)

cyanogen

potassium cyanide (151-50-8)

allyl chloride (107-05-1)

allyl iodide (556-56-9)