



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.

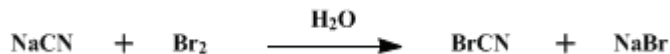
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 2, p.150 (1943); Vol. 11, p.30 (1931).

CYANOGEN BROMIDE



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1. Procedure

A 2-l. round-bottomed flask, surrounded by an ice-water bath and provided with a stirrer, a separatory funnel, and an outlet tube, is set up in a good hood. To the flask are added 500 g. (160 cc., 3.1 moles) of bromine and 50 cc. of water (Note 1). To the stirred mixture is added gradually a solution of 170 g. of sodium cyanide (3.5 moles) in 1.2 l. of warm water. The temperature of the reaction mixture is kept below 30°. When the reaction is complete (about two hours or less) the cyanogen bromide is distilled from a steam bath, using a 500-cc. flask (Note 2) as a receiver. The distillate is warmed with about 100 g. of anhydrous calcium chloride, filtered, and again distilled, preferably with the distilling flask used as a receiving vessel connected directly to the flask from which the cyanogen bromide is being distilled. The product boils at 60–62°. It is melted in the receiver (Note 3) (Hood) and poured into a warm tared bottle. The yield of white crystalline solid (Note 4) melting at 49–51° is 239–280 g. (73–85 per cent of the theoretical amount).

2. Notes

1. Water is used to decrease the volatilization of the bromine.
2. It is desirable to have the receiving flask close to the distilling flask because cyanogen bromide will clog a tube which is too small in diameter or too long.
3. Because of the toxic nature of the product it is best to wear a gas mask while transferring the molten product.
4. Cyanogen bromide does not keep well and may at times even become explosively unstable on standing. It is preferable to prepare it just before using.

3. Discussion

Cyanogen bromide has been prepared from an aqueous solution of potassium cyanide and bromine at 0°;¹ by the action of bromine on an alkali cyanide in the presence of carbon tetrachloride and acetic acid;² and from bromine and moist mercuric cyanide.³ Detailed directions have been published by Slotta for the preparation from bromine and aqueous potassium cyanide.¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 608](#)
- [Org. Syn. Coll. Vol. 7, 435](#)

References and Notes

1. Langlois, *Ann. chim. phys.* (3) **61**, 482 (1861); Scholl, *Ber.* **29**, 1823 (1896); Baum, *ibid.* **41**, 523 (1908); Slotta, *ibid.* **67**, 1028 (1934).
 2. National Aniline and Chemical Company, U. S. pat. 1,938,324 [C. A. **28**, 1148 (1934)].
 3. Sérullas, *Ann. chim. phys.* (2) **34**, 100 (1827).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

calcium chloride (10043-52-4)

acetic acid (64-19-7)

sodium cyanide (143-33-9)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

potassium cyanide (151-50-8)

Cyanogen bromide (506-68-3)

mercuric cyanide (592-04-1)