



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.

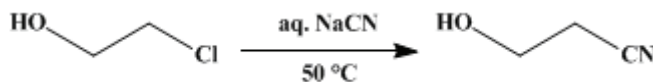
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.256 (1941); Vol. 3, p.57 (1923).

ETHYLENE CYANOHYDRIN

[Hydracrylonitrile]



Submitted by E. C. Kendall and B. McKenzie.

Checked by H. T. Clarke and W. M. Sperry.

1. Procedure

In a 5-l. flask is placed 612 g. (12.5 moles) of finely powdered [sodium cyanide](#) (passed through a meat grinder and then sifted through a 20-mesh sieve) ([Note 1](#)); the flask is equipped with a thermometer in a well, an efficient stirrer, and a reflux condenser ([Note 2](#)). The whole vessel is then set in a water bath into which warm and cold water can be run at will and if necessary rapidly removed.

A mixture of 250 cc. of water and 1 kg. (807 cc., 12.4 moles) of pure [ethylene chlorohydrin](#) (b.p. 126–127°) is then added, the stirring is started, and the temperature of the mixture raised to 45° by external application of warm water. At this point the warm water is rapidly removed ([Note 3](#)) and the temperature of the contents of the flask carefully held at 45° by jacketing with water at a suitable temperature (33–35°). After the mixture has been held at 45° for one hour it is allowed to warm up to 48° by allowing the temperature of the water bath to rise about 2°. After an hour at 48° the temperature is raised to 50° and held at this point until the reaction is over; it is necessary to raise the temperature of the bath gradually, and the end of the reaction is noted when the bath temperature reaches 50°. A period of four and one-half to five hours is necessary for this last stage.

Cold water is now placed in the water bath, while the stirrer is kept always in motion, and the temperature of the mixture is reduced to 20–22°. The mass is then filtered by suction and the [sodium chloride](#) sucked as dry as possible. This is then washed with about 800 cc. of [acetone](#) in small quantities, the washings being collected separately, and then transferred to a flask from which the [acetone](#) and water are distilled off with the use of a short fractionating column until the temperature of the vapor reaches 90°. The residue in the flask is then cooled and again filtered from a further small quantity of [sodium chloride](#) which separates during the distillation, the filtrate being added to the main product ([Note 4](#)).

This is then distilled under reduced pressure from an oil bath, and the fraction boiling at 107–109°/12 mm. (116–118°/20 mm.) is collected as pure material. The yield is 700–705 g. (79–80 per cent of the theoretical amount). There is practically no residue beyond a little salt; the foreruns consist of water, a small amount of unchanged [ethylene chlorohydrin](#), and some [ethylene cyanohydrin](#).

2. Notes

1. The [sodium cyanide](#) should be finely powdered since it never completely enters into solution, and any lumps present would run the risk of becoming coated over with [sodium chloride](#). For the same reason, the stirring must be vigorous throughout the operation.
2. Under the correct conditions no appreciable amount of [hydrogen cyanide](#) escapes from the reflux condenser, but it is wise to carry out the reaction under a hood, or to lead a tube from the top of the condenser into the open air or to a gas-absorption trap ([Fig. 7 on p. 97](#)).
3. It is most important that the temperature of the reaction mixture be not allowed to rise prematurely, since if it reaches 50° during the early stages the reaction velocity increases so rapidly that the contents are likely to boil out of the flask. For the same reason it appears necessary that a certain ratio between reacting mass and cooled surface be not exceeded. Runs of twice the above size have been carried out in a 5-l. flask without mishap, but temperature control was difficult and these conditions are extremely hazardous. A run of 4 kg. of [ethylene chlorohydrin](#) in a 12-l. flask was attempted, but rapidly went out

of control.

4. When the reaction has been carried out exactly as described, the final product before distillation is very nearly colorless; if the temperature has been allowed to rise too high, a brown color is produced and **ammonia** is formed, with corresponding decrease in yield.

3. Discussion

Ethylene cyanohydrin can be prepared from ethylene oxide and anhydrous hydrogen cyanide;¹ from ethylene oxide and calcium cyanide in aqueous solution at 10–20°;² and from ethylene chlorohydrin and alkali cyanide in the absence of a solvent by heating to 100° in a closed vessel,³ by boiling the reagents in 50 per cent aqueous-alcoholic solution,⁴ by adding a concentrated aqueous solution of potassium or sodium cyanide to a boiling solution of the chlorohydrin in absolute alcohol,⁵ or in aqueous solution at 45°.⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 131](#)
- [Org. Syn. Coll. Vol. 1, 321](#)

References and Notes

1. Erlenmeyer, Ann. **191**, 270 (1878); Wislicenus, Ann. **167**, 346 (1873).
2. I. G. Farbenind. A.-G., Ger. pat. 561,397 [C. A. **27**, 998 (1933)].
3. Wislicenus, Ann. **128**, 4 (1863).
4. Erlenmeyer, Ann. **191**, 268 (1878).
5. Moureu, Bull. soc. chim. (3) **9**, 426 (1893); Moureu and Brown, *ibid.* (4) **27** 902 (1920); Jacobs and Heidelberger, J. Am. Chem. Soc. **39**, 1465 (1917).
6. Bauer, U. S. pat. 1,388,016 [C. A. **15**, 4011 (1921)].

Appendix

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

alkali cyanide

potassium or sodium cyanide

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

[ammonia](#) (7664-41-7)

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

[sodium chloride](#) (7647-14-5)

[hydrogen cyanide](#) (74-90-8)

[acetone](#) (67-64-1)

[Ethylene oxide](#) (75-21-8)

Ethylene cyanohydrin,
Hydracrylonitrile (109-78-4)

ethylene chlorohydrin (107-07-3)

calcium cyanide (592-01-8)