



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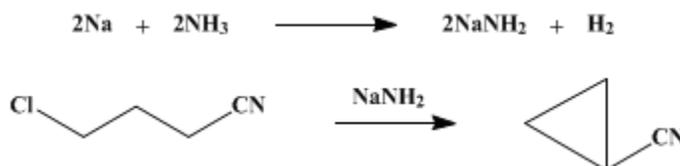
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.223 (1955); Vol. 23, p.20 (1943).

CYCLOPROPYL CYANIDE

[Cyclopropane, cyano-]



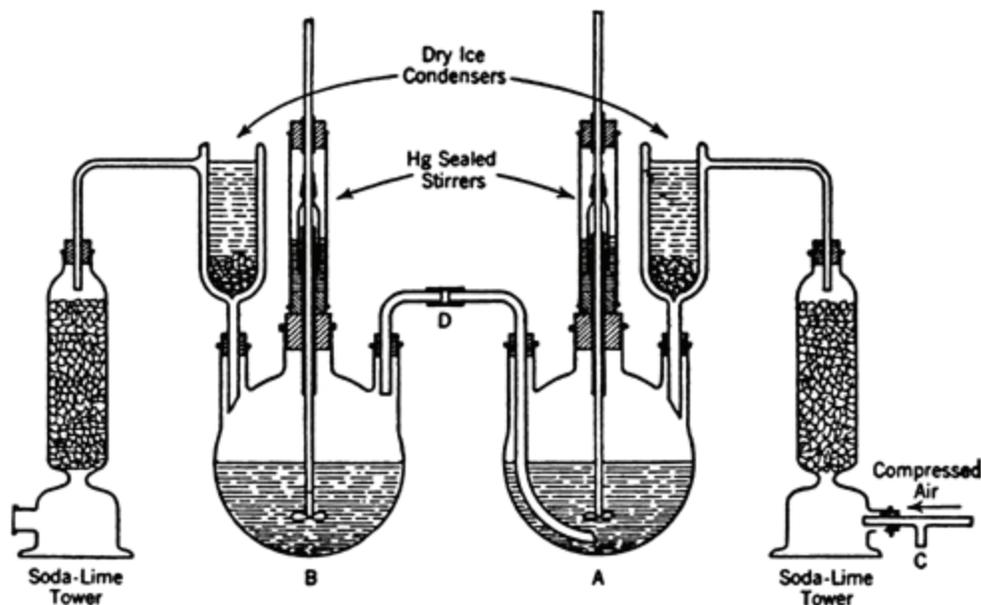
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1. Procedure

The apparatus shown in Fig. 10 is assembled in a good hood. One liter of liquid ammonia and 0.5 g. of hydrated ferric nitrate are placed in the 2-l. three-necked flask *A*, which is equipped with a stirrer and a special reflux condenser cooled with Dry Ice. This condenser is attached to a soda-lime tower which is connected to a source of compressed air through the T-tube *C*. Over a period of about 45 minutes, 92 g. (4 gram atoms) of clean sodium shavings is added to the liquid ammonia, and the mixture is stirred until the blue color disappears (1–2 hours).

Fig. 10.



In the similarly equipped 5-l. three-necked flask *B* are placed 1.5 l. of liquid ammonia and 440 g. (4.25 moles) of γ -chlorobutyronitrile [*Org. Syntheses Coll. Vol. 1, 156 (1941)*]. The flasks are connected by means of the 12-mm. glass tube *D* reaching to the bottom of the sodamide flask *A* and extending 1 cm. through the rubber stopper in one neck of flask *B*. Vigorous stirring is maintained in both flasks while the sodamide suspension is slowly forced over into the reaction flask in small portions (*Caution! (Note 1)*) by means of air pressure applied through *C*; the rate of addition is controlled by placing the finger over the by-pass in the T-tube. At first the reaction is violent, and only small amounts of the sodamide solution should be added. The addition is continued at such a rate that the total time required for addition of all the sodamide solution is 1–1.5 hours. The sodamide flask is rinsed with 300 ml. of liquid ammonia, and the washings are added to the reaction mixture, after which stirring is continued for 2 hours. During the second hour, addition of Dry Ice to the reflux condenser is

discontinued, and the ammonia is permitted to evaporate slowly. At the end of the 2-hour stirring period, the inlet tube is replaced by a dropping funnel and 1 l. of dry ether is slowly added (Note 2). The reaction mixture is quickly filtered through a sintered-glass funnel, and the filter cake is washed with two 200-ml. portions of dry ether (Note 3). The ammonia and ether are removed by distillation on a water bath through a packed column (Note 4). The residue is then distilled through the column under the pressure of a water pump (Note 5). The yield of cyclopropyl cyanide boiling at 69–70°/80 mm. (75–76°/95 mm.) is 149–152 g. (52–53% based upon γ -chlorobutyronitrile) (Note 6) and (Note 7). The pressure is then reduced, and the unchanged γ -chlorobutyronitrile is collected at 93–96°/26 mm. It amounts to 52–62 g.

2. Notes

1. The reaction is very vigorous, and addition of the sodamide solutions in large portions must be avoided. The use of stopcocks or pinch clamps to regulate the addition is not recommended.
2. Very little cyclopropyl cyanide is obtained unless the ether is added *before* complete evaporation of the ammonia.
3. The mixture may be permitted to stand at this point and the ammonia allowed to evaporate spontaneously under a hood.
4. The Carborundum column described in *Org. Syntheses*, **20**, 96, is quite satisfactory.
5. It is desirable to interpose a Dry Ice trap between the receiver and the pump in order to prevent loss of the nitrile, and too low a pressure should not be used.
6. The submitter reports that an equivalent number of moles of γ -bromobutyronitrile or a mixture of γ -chloro- and γ -bromobutyronitrile may be substituted for γ -chlorobutyronitrile. If the bromo compound is used the reaction mixture should be refluxed 6 hours and it is necessary to filter off the sodium bromide just before the final vacuum distillation.
7. This yield is based upon the γ -chlorobutyronitrile taken. When the recovered γ -chlorobutyronitrile (52–62 g.) is taken into account, the yield of cyclopropyl cyanide is about 60%.

3. Discussion

Cyclopropyl cyanide has been prepared by the repeated distillation of γ -chlorobutyronitrile over powdered potassium hydroxide,^{1,2,3,4,5} or over a mixture of sodium hydroxide and alumina.⁶ The preparation, on a small scale, of cyclopropyl cyanide from γ -chlorobutyronitrile by action of sodium in liquid ammonia, or of sodium suspended in ether, has been described.⁷ The present directions are based upon those given by Schlatter.⁸

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 5*, 12

References and Notes

1. Henry, *Rec. trav. chim.*, **18**, 228 (1898).
 2. Dalle, *Bull. acad. roy. Belg.*, **1902**, 36–79 (*Chem. Zentr.*, **1902**, I, 913).
 3. Bruylants and Stassens, *Bull. acad. roy. Belg.*, **1921**, 702–19 [*C. A.*, **17**, 2872 (1923)].
 4. von Braun, Fussgänger, and Kühn, *Ann.*, **485**, 210 (1925).
 5. Nicolet and Sattler, *J. Am. Chem. Soc.*, **49**, 2068 (1927).
 6. Cloke, *J. Am. Chem. Soc.*, **51**, 1180 (1929).
 7. Cloke, Anderson, Lachman, and Smith, *J. Am. Chem. Soc.*, **53**, 2791 (1931).
 8. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941).
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Appendix

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

alumina

γ -chloro- and γ -bromobutyronitrile

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium bromide (7647-15-6)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

γ -Chlorobutyronitrile (628-20-6)

sodamide (7782-92-5)

ferric nitrate

Cyclopropyl cyanide,
Cyclopropane, cyano- (5500-21-0)

γ -bromobutyronitrile (5332-06-9)