



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.

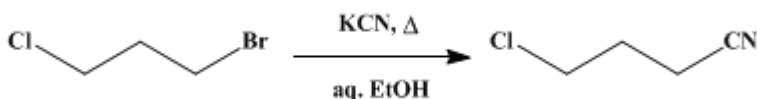
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.156 (1941); Vol. 8, p.52 (1928).

γ -CHLOROBUTYRONITRILE

[Butyronitrile, γ -chloro-]



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1. Procedure

In a 2-l. three-necked, round-bottomed flask, fitted with a stirrer, a reflux condenser and a separatory funnel are placed 82 g. (1.2 moles) of [potassium cyanide](#) (95 per cent) ([Note 1](#)) and 100 cc. of water. The mixture is warmed and stirred until the [cyanide](#) is completely dissolved. To this solution is added 350 cc. of 95 per cent [alcohol](#), followed by 158 g. (1 mole) of [trimethylene chlorobromide](#) ([Note 2](#)), and the mixture is heated under a reflux condenser (best on a water bath) with stirring for about one and one-half hours.

The solution is cooled and then diluted with 450 cc. of water. The oily layer of [chloronitrile](#) is collected in about 80 cc. of [chloroform](#) and separated from the water solution. The [chloroform](#) solution is washed with about 125–150 cc. of [calcium chloride](#) solution (prepared by adding one volume of water to an equal volume of a saturated solution of crystallized [calcium chloride](#)) and once with 125–150 cc. of water, and then dried over fused [calcium chloride](#).

The dried solution is then fractionally distilled in a modified 100-cc. Claisen flask ([p. 130](#)). The [chloroform](#) is removed by distilling at ordinary pressure until the temperature reaches 120° ([Note 3](#)). The remainder may be fractionated under ordinary pressure but it is better to use reduced pressure. After two or three distillations the yield of pure product boiling at 93–96°/26 mm. ([Note 4](#)) and ([Note 5](#)) is 42–49 g. (60–70 per cent of the theoretical amount based on the chlorobromide used, or 40–47 per cent based on the total amount of chlorobromide taken) ([Note 5](#)) and ([Note 6](#)).

2. Notes

1. An equivalent amount (58 g., 1.2 moles) of [sodium cyanide](#) dissolved in 90 cc. of water may be used instead of the potassium salt without materially altering the yields.
2. The [trimethylene chlorobromide](#) used boiled at 142–147°. It may be prepared in 75–85 per cent yields from [trimethylene chlorohydrin](#) ([p. 533](#)) by the general method for the preparation of alkyl bromides described on [p. 25](#). Directions are also available¹ for its preparation in higher yields by the action of [phosphorus tribromide](#) on [trimethylene chlorohydrin](#).
3. The [chloroform](#) fraction has a very strong odor of [isonitrile](#). Only a trace is noted in the redistilled product.
4. When the distillation is carried out under ordinary pressures (about 745 mm.) the product boils at 194–197°.
5. The lower-boiling fraction is mainly unchanged [trimethylene chlorobromide](#) and amounts to 15–20 g. It may be refractionated or used directly in a subsequent run. The high-boiling residue is mainly [trimethylene cyanide](#). If the residues from several runs are combined and redistilled, an average of 6–7 g. per run of product boiling at 160–165°/26 mm. is obtained.
6. Larger runs have been made and the yields are proportional; thus a five-mole run gives 210–245 g. of [chlorobutyronitrile](#) and 30–35 g. of [trimethylene cyanide](#).

3. Discussion

γ -Chlorobutyronitrile has always been prepared by the action of [potassium cyanide](#) on [trimethylene](#)

chlorobromide.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 25
- Org. Syn. Coll. Vol. 3, 221
- Org. Syn. Coll. Vol. 3, 223

References and Notes

1. Cloke, Anderson, Lachmann and Smith, J. Am. Chem. Soc. **53**, 2794 (1931).
 2. Henry, Compt. rend. **101**, 1158 (1885); Bull. soc. chim. (2) **45**, 341 (1886); Gabriel, Ber. **23**, 1771 (1890) and **42**, 1252 (1909); Conant, Segur and Kirner, J. Am. Chem. Soc. **46**, 1884 (1924); Dewael, Bull. soc. chim. Belg. **39**, 87 (1930).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

potassium salt

alcohol (64-17-5)

calcium chloride (10043-52-4)

chloroform (67-66-3)

sodium cyanide (143-33-9)

phosphorus tribromide (7789-60-8)

cyanide,
isonitrile (57-12-5)

potassium cyanide (151-50-8)

γ -Chlorobutyronitrile,
Butyronitrile, γ -chloro-,
chlorobutyronitrile (628-20-6)

Trimethylene chlorobromide (109-70-6)

chloronitrile (7790-93-4)

Trimethylene chlorohydrin (627-30-5)

Trimethylene cyanide (544-13-8)