



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.

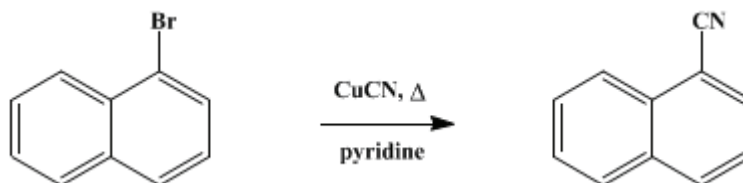
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.631 (1955); Vol. 21, p.89 (1941).*

## **$\alpha$ -NAPHTHONITRILE**

### **[1-Naphthonitrile]**



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### **1. Procedure**

In a dry 200-ml. flask fitted with a ground-joint reflux condenser and protected from moisture by a calcium chloride tube are put 66 g. (0.32 mole) of  $\alpha$ -bromonaphthalene (Note 1), 35 g. (0.39 mole) of dry powdered cuprous cyanide (Note 2), and 30 ml. of pyridine (Note 3) in the order mentioned. This mixture is heated in a Wood's metal bath (Note 4) at 215–225° for 15 hours. The resulting dark brown solution is poured while still hot (about 100°) into a flask containing 150 ml. of aqueous ammonia (sp. gr. 0.90) and 150 ml. of water. About 140 ml. of benzene is added, and the flask is stoppered and shaken until all the lumps have disintegrated. After the mixture has cooled to room temperature, 100 ml. of ether is added and the mixture is filtered (Note 5). The filtrate is transferred to a 1-l. separatory funnel, and the aqueous layer is separated (Note 6). The ether-benzene layer is washed successively with (a) four 100-ml. portions of dilute aqueous ammonia (Note 7), (b) two 100-ml. portions of 6 N hydrochloric acid (Note 8), (c) two 100-ml. portions of water, and (d) two 100-ml. portions of saturated sodium chloride solution. The ether and benzene are removed by distillation from a water bath, and the residue is distilled under reduced pressure from a 125-ml. modified Claisen flask. The temperature rises rapidly, and the yield of colorless  $\alpha$ -naphthonitrile, b.p. 173–174°/27 mm. (166–169°/18 mm.), is 40–44 g. (82–90%) (Note 9) and (Note 10).

### **2. Notes**

1. The  $\alpha$ -bromonaphthalene was redistilled just before use and the fraction boiling at 153–154°/22 mm. taken.
2. "Baker's Analyzed" cuprous cyanide (powdered) was used. The cuprous cyanide must be dry.
3. Pure pyridine dried over barium oxide was used. A considerable amount of heat is liberated on addition of the pyridine to the mixture.
4. A fused salt bath consisting of 8.5 parts (by weight) of sodium nitrite and 10 parts of potassium nitrate has a melting point of about 140° and may replace the metal bath.
5. The cuprammonium solution attacks filter paper and hence this solution is best filtered through a fritted-glass filter. Two layers of ordinary toweling cloth on a Büchner funnel may also be used.
6. It is occasionally necessary to add an additional 50–100 ml. of ether to facilitate separation.
7. If the final ammoniacal wash solution is not colorless, the ether/benzene solution should be washed with additional 100-ml. portions of dilute aqueous ammonia.
8. If a precipitate separates during this operation it should be removed by filtration.
9. The yields vary with the quality of the cuprous cyanide. One lot of this reagent gave yields of only 60–75%. Larger amounts may be run, but the amount of pyridine used should be reduced to decrease the reflux. For a 2-mole run, 160 ml. of pyridine was satisfactory. The yield of the large runs was 81%.
10.  $\alpha$ -Chloronaphthalene (b.p. 144–146.5°/29 mm.) may be used in place of  $\alpha$ -bromonaphthalene, but 24 hours' heating at 245–250° is required. The yields are about the same.

### **3. Discussion**

$\alpha$ -Naphthonitrile has been prepared from  $\alpha$ -naphthylamine by the Sandmeyer reaction,<sup>1</sup> from  $\alpha$ -chloronaphthalene,<sup>2</sup> from  $\alpha$ -bromonaphthalene<sup>3</sup> by heating with cuprous cyanide, by heating the sodium salt of  $\alpha$ -naphthalenesulfonic acid with sodium cyanide<sup>4</sup> or with potassium ferrocyanide, iron, and ferric oxide,<sup>5</sup> by heating  $\alpha$ -naphthamide with phosphorus pentachloride<sup>6</sup> or with sodium chloroaluminate,<sup>7</sup> and by distilling  $\alpha$ -naphthoic acid with dicyandiamide.<sup>8</sup>

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## References and Notes

1. Rupe and Brentano, *Helv. Chim. Acta*, **19**, 581 (1936); McRae, *J. Am. Chem. Soc.*, **52**, 4550 (1930); Clarke and Read, *J. Am. Chem. Soc.*, **46**, 1001 (1924).
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  3. Newman, *J. Am. Chem. Soc.*, **59**, 2472 (1937).
  4. Whitmore and Fox, *J. Am. Chem. Soc.*, **51**, 3363 (1929).
  5. Wahl, Goedkoop, and Heberlein, *Bull. soc. chim. France*, (5) **6**, 533 (1939).
  6. Blicke, *J. Am. Chem. Soc.*, **49**, 2848 (1927).
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## Appendix

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

$\alpha$ -naphthylamine

$\alpha$ -bromonaphthalene

sodium chloroaluminate

dicyandiamide

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

iron (7439-89-6)

sodium cyanide (143-33-9)

sodium chloride (7647-14-5)

barium oxide

Cuprous Cyanide (544-92-3)

sodium nitrite (7632-00-0)

pyridine (110-86-1)

$\alpha$ -Bromonaphthalene (90-11-9)

potassium ferrocyanide

potassium nitrate (7757-79-1)

ferric oxide (1309-37-1)

$\alpha$ -Naphthoic acid (86-55-5)

$\alpha$ -Naphthonitrile,  
1-Naphthonitrile (86-53-3)

sodium salt of  $\alpha$ -naphthalenesulfonic acid (130-14-3)

$\alpha$ -naphthamide (2243-81-4)

$\alpha$ -Chloronaphthalene (90-13-1)