Organic Syntheses

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.*

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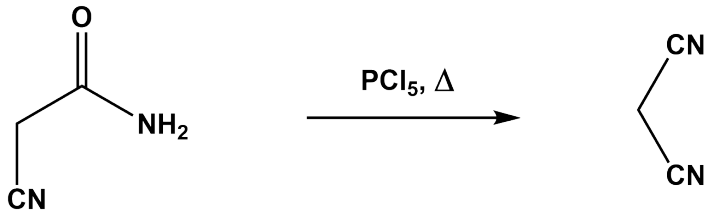
*Organic Syntheses, Coll. Vol. 2, p.379 (1943); Vol. 10, p.66 (1930).*

# MALONONITRILE




Submitted by B. B. Corson, R. W. Scott, and C. E. Vose.
Checked by C. S. Marvel and J. Harmon.

## 1. Procedure

One hundred fifty grams (1.8 moles) of pure cyanoacetamide (Org. Syn. Coll. Vol. I, **1941**, 179) is thoroughly mixed in a large (20-cm.) mortar with 150 g. (0.7 mole) of phosphorus pentachloride (Note 1). This mixture is transferred (Note 2) as quickly as possible to a 1-l. Claisen flask equipped with a 360° thermometer and an air-intake tube (Note 3). The Claisen flask is connected by means of a double-length air condenser to a 250-cc. filter flask which in turn is connected to a water pump (Note 4) through a manometer.

After the system has been evacuated to about 30 mm. of mercury, the Claisen flask is immersed in a boiling water bath. The mixture melts and its color deepens to orange. Boiling commences in about fifteen minutes, before the solid is completely melted, and the pressure rises to about 150 mm. owing to the liberation of hydrogen chloride and phosphorus oxychloride (Note 5). When the evolution of gas has slackened, as indicated by the fall of pressure and the less vigorous boiling of the reaction mixture (thirty to thirty-five minutes), the receiver is changed. The distilling flask is removed from the boiling water bath, wiped dry, and immersed in an oil bath at 140° (Note 6); the fresh receiver is placed in ice water.

The malononitrile begins to distil at 113°/30 mm. (125°/50 mm.). The temperature of the oil bath is slowly raised over a period of twenty-five minutes to 180° (Note 7) and the nitrile collected between 113° and 125°. When the distillation has almost ceased, the oil bath is removed so as to prevent discoloration of the product (Note 8). The yield of crude nitrile is 80–95 g. (67–80 per cent of the theoretical amount) (Note 9). The nitrile may be purified by vacuum distillation (Note 10) with about 10 per cent loss; it is collected between 113° and 120°/30 mm. One distillation yields a water-clear liquid, which quickly freezes to an ice-like solid (Note 11) melting at 28–30°. The product has a faint odor resembling that of acetamide.

## 2. Notes

1. The weights of the reactants correspond to the ratio of 5 molecules of amide to 2 molecules of pentachloride. The use of larger proportions of phosphorus pentachloride leads to lower yields.[1]
The phosphorus pentachloride should be of good quality—a dry solid.
2. This transfer is greatly facilitated by the use of a 15-cm. (6-inch) glass funnel whose stem has been cut off and the hole enlarged to almost the size of the neck of the Claisen flask. The mixture is emptied into the body of the funnel and pushed through the large hole by means of a glass rod. A gas mask should be worn, for any considerable breathing of the fumes brings on a harsh cough which may last for

several days.
3. To avoid plugging, the air-intake tube is not drawn out to a capillary.
4. An oil pump cannot be used because of the corrosive acid fumes.
It is reported that a single water pump is usually unable to remove the evolved gases fast enough, with the result that some material is carried over mechanically with the foam. If two water pumps in parallel are used, this difficulty is overcome. (C. F. H. Allen, private communication.)
5. Unless the phosphorus oxychloride is to be recovered, it is advisable to allow it to be carried away by the suction. This is easily accomplished if the receiver is not cooled.
6. If the initial temperature of the oil bath is below 140°, the nitrile distils too slowly (with consequent lowering of yield); if the temperature is above 140°, the nitrile distils too rapidly, some condenses in the rubber tubes leading to the pump and clogs the line.
The flask should be immersed as far as possible in the oil (to within about 100 mm. of the top of the flask). A 1-gal. enamelware coffee-pot makes an excellent oil bath. An ordinary soldered vessel will not stand the temperature.
7. The temperature of the oil bath must not rise much above 180°, else the distillate becomes colored and violent bumping is liable to occur. The distillate should not be allowed to solidify in the condenser. This is most likely to occur during the first part of the distillation. The solid is easily melted by heating with a small flame.
8. The residue in the Claisen flask can be softened by water and broken up with a rod. The small amount remaining is easily removed with concentrated nitric or, preferably, concentrated sulfuric acid.
9. The keynote to success in this preparation is speed. Malononitrile is a sensitive substance and it must be removed from the reaction mixture as rapidly as possible. After experience with one or two runs the yields will consistently be better than 67 per cent.
10. Malononitrile can be distilled in small amounts (50 cc. or so) at ordinary pressure; the boiling point is around 220°. However, the longer heating necessary with larger amounts is likely to cause violent decomposition: the liquid darkens, boils spontaneously, and finally spurts from the flask in a cloud of white fumes and burning liquid; the latter partially solidifies to a brittle red solid.
11. Nitrogen determinations indicate a purity of 99.5 per cent. The product remains colorless for at least one year if stored in brown bottles protected from the light. If kept in ordinary bottles and exposed to the light, the nitrile quickly darkens.
12. This work was aided by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

## 3. Discussion

Malononitrile has been prepared by the action of phosphorus pentachloride on cyanoacetamide,[1] and by the action of phosphorus pentoxide on malonamide[2] or cyanoacetamide.[3] The preparation using the pentoxide is much less satisfactory than that given above.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 535

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## References and Notes

1. Hesse, Am. Chem. J. **18**, 726 (1896).
2. Henry, Compt. rend. **102**, 1394 (1886).
3. Henry, ibid. **102**, 1395 (1886).

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

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

Acetamide (60-35-5)

phosphorus pentachloride (10026-13-8)

nitrogen (7727-37-9)

mercury (7439-97-6)

Phosphorus Oxychloride (21295-50-1)

CYANOACETAMIDE (107-91-5)

malonamide (108-13-4)

Malononitrile (109-77-3)

phosphorus pentoxide (1314-56-3)