



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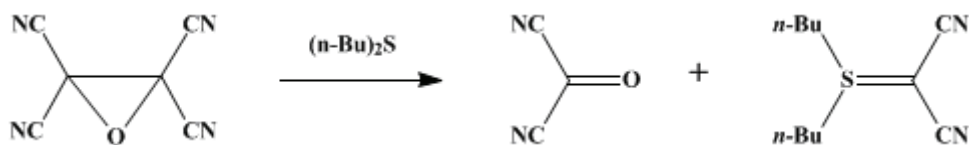
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.268 (1988); Vol. 51, p.70 (1971).

CARBONYL CYANIDE

[Propanedinitrile, oxo-]



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1. Procedure

Caution! Carbonyl cyanide and water react with explosive violence, forming hydrogen cyanide and carbon dioxide. This preparation should be carried out in a good hood with shielding, and rubber gloves should be worn.

A 500-ml., three-necked flask equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel, a thermometer, and a 25-cm. Vigreux column attached to a trap cooled in an acetone–dry ice mixture is charged with 100 ml. of **diethyl phthalate** (Note 1) and 43 g. (0.30 mole) of **tetracyanoethylene oxide** (Note 2). The dropping funnel is charged with 44 g. (0.30 mole) of distilled *n*-butyl sulfide, the pressure is reduced to 5–20 mm. with a water aspirator, and the reaction flask is warmed with a 50° water bath. The *n*-butyl sulfide is added dropwise with stirring over 20–25 minutes, and the internal temperature is maintained at 50 ± 2° by controlling the temperature of the water bath. The reaction is exothermic at the start, but it is necessary to supply heat toward the end of the addition. The internal temperature is increased to 80° over 10–15 minutes after the sulfide has been added. The vacuum on the system is released by the introduction of **nitrogen**. The solid **carbonyl cyanide** that has collected in the trap is allowed to warm to room temperature under **nitrogen**, and 2 g. of **tetracyanoethylene oxide** (Note 3) and a boiling stone are added. The mixture is then warmed to 50°, and the product is distilled under reduced pressure (5–20 mm.) into a second trap cooled in an acetone–dry ice mixture. Another portion of **tetracyanoethylene oxide** (1 g.) is added to the distillate, and the **carbonyl cyanide** is distilled, again under reduced pressure (5–20 mm.), into a distillation flask cooled in acetone–dry ice mixture. Fractionation of the distillate through a 20-cm. column packed with glass helices gives 20.8–21.8 g. (86–91%) (Note 4) of faintly yellow **carbonyl cyanide**, b.p. 65–66° (Note 5), (Note 6), and (Note 7).

2. Notes

1. The **diethyl phthalate** is freed of traces of water and **ethanol** by distilling about 5% of it under reduced pressure, b.p. 185° (20 mm.) and then cooling the residue with protection from moisture. Moisture must be excluded because **carbonyl cyanide** reacts vigorously with water.
2. **Tetracyanoethylene oxide** was prepared as described in *Org. Synth.*, **Coll. Vol. 5**, 1007 (1973).
3. The distillate is treated with **tetracyanoethylene oxide** to remove the small amount of *n*-butyl sulfide that codistills with **carbonyl cyanide**.
4. The yield is based on the amount of **tetracyanoethylene oxide** initially charged.
5. There is very little if any low-boiling material when the reaction is carried out as described and care is taken to have the apparatus dry and exclude moisture.
6. GC analyses of various cuts indicate essentially pure **carbonyl cyanide** with traces of **hydrogen cyanide** and **carbon dioxide**. Both are hydrolysis products of **carbonyl cyanide** and probably are formed because of traces of moisture on the column.
7. **Carbonyl cyanide** has m.p. –38°, n_D^{19} 1.3923.²

3. Discussion

The procedure described is that of Linn, Webster, and Benson.³ Carbonyl cyanide has previously been prepared by the pyrolysis of the diacetyl derivative of diisonitrosoacetone, a multistep process that suffers from low yield, lack of reproducibility, and risk of explosion.² The present procedure provides a convenient high-yield synthesis of carbonyl cyanide.

Carbonyl cyanide reacts with alcohols and phenols, giving cyanofomate esters;⁴ with primary and secondary amines, giving cyanofomamides; with *N,N*-dimethylaniline, giving bis[4-(dimethylamino)phenyl]malononitrile; and with pyrrole, giving 2-(cyanoformyl)pyrrole.⁵ With olefins of the type C=C-CH₂, products with structures C=CC-C(CN)₂OH, C=CC-COCN, and C=CC-C(CN)₂OCOCN are obtained, depending on the nature of the olefin and the reaction conditions.⁶ Carbonyl cyanide also undergoes Diels-Alder reactions with some conjugated dienes, yielding dicyanodihydropyrans.⁷

References and Notes

1. Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware 19898.
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3. W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965); W. J. Linn, U.S. Pat. 3,115,517 (1963) [*Chem. Abstr.*, **60**, 7919a (1964)].
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Appendix

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

ethanol (64-17-5)

hydrogen cyanide (74-90-8)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

N,N-dimethylaniline (121-69-7)

Pyrrole (109-97-7)

diethyl phthalate (84-66-2)

Tetracyanoethylene oxide (3189-43-3)

carbonyl cyanide,
Propanedinitrile, oxo- (1115-12-4)

diisonitrosoacetone

bis[4-(dimethylamino)phenyl]malononitrile

2-(cyanoformyl)pyrrole

n-butyl sulfide (544-40-1)