



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.

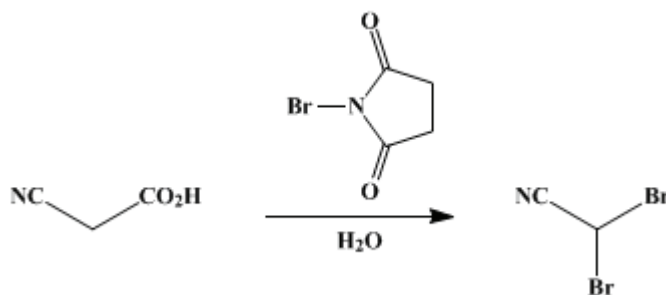
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.254 (1963); Vol. 38, p.16 (1958).*

## DIBROMOACETONITRILE

[Acetonitrile, dibromo-]



Submitted by James W. Wilt and James L. Diebold<sup>1</sup>.

Checked by B. C. Mckusick and H. E. Knipmeyer.

### 1. Procedure

A solution of 63.8 g. (0.75 mole) of [cyanoacetic acid](#) ([Note 1](#)) in 750 ml. of cold water is placed in a 2-l. beaker. [N-Bromosuccinimide](#) (267 g., 1.5 moles) ([Note 2](#)) is added in portions with good mechanical stirring over a period of about 6 minutes ([Note 3](#)). The slightly exothermic reaction which attends the separation of the [dibromoacetonitrile](#) as a heavy oil is completed in about 20 minutes, after which time the beaker is placed in an ice bath and allowed to cool for 2 hours ([Note 4](#)).

The precipitated [succinimide](#) is collected on a large Büchner funnel atop a 2-l. filter flask and is washed with six 50-ml. portions of [methylene chloride](#). The lower organic layer in the filtrate is separated from the aqueous phase, which is extracted with two 25-ml. portions of [methylene chloride](#). The organic layer and the extracts are combined, washed vigorously with 50 ml. of a 5% [sodium hydroxide](#) solution ([Note 5](#)) and three 80-ml. portions of water, and dried over 10 g. of anhydrous [sodium sulfate](#) for several hours in a flask wrapped with aluminum foil ([Note 6](#)).

The colorless dried oil is distilled through a 45-cm. Widmer column ([Note 7](#)). Most of the [methylene chloride](#) is removed by heating the contents of the distillation pot to 75° at atmospheric pressure. The pressure is then lowered to about 20 mm., and 112–129 g. (75–87%) of [dibromoacetonitrile](#) is collected as a colorless oil, b.p. 70–72°/20 mm.,  $n_D^{25}$  1.540–1.542,  $d_4^{20}$  2.369 ([Note 8](#)) and ([Note 9](#)).

### 2. Notes

- Commercial [cyanoacetic acid](#) (Eastman Kodak Company), m.p. 67–71.5°, about 98% pure, was found satisfactory for this preparation.
- [N-Bromosuccinimide](#) obtained from Matheson, Coleman and Bell, Inc., as well as from Arapahoe Chemicals, Inc., was used as received. The [N-chlorosuccinimide](#) ([Note 9](#)) was commercial material from Arapahoe Chemicals, Inc.
- The [N-bromosuccinimide](#) should be added as rapidly as possible consistent with the foaming produced by evolution of [carbon dioxide](#).
- About one-third of the [succinimide](#) (50–53 g.) precipitates from the solution during the cooling period, thus rendering the subsequent purification of the nitrile easier. Sometimes the solution must be seeded to start the precipitation. The checkers found it necessary to store the mixture in a refrigerator over-night in order to obtain 50–53 g. of [succinimide](#).
- The basic aqueous phase becomes pink through action of the base on [dibromoacetonitrile](#).
- Pure [dibromoacetonitrile](#) is fairly stable to air and light, but traces of basic impurities cause it to become discolored ([Note 5](#)). Protective shielding retards this coloration.
- Unless an efficient column is used, some nitrile distils over with the [methylene chloride](#). The

checkers used a 120-cm. spinning-band column.

8. The product shows good shelf stability, but, as a precautionary measure, it is best stored under nitrogen in a sealed brown vessel. Dichloroacetonitrile (Note 9) is less sensitive and may be stored in an ordinary glass-stoppered brown bottle.

9. In exactly the same fashion, from 63.8 g. (0.75 mole) of cyanoacetic acid and 200.3 g. (1.5 moles) of N-chlorosuccinimide there may be obtained 45–54 g. (55–65%) of colorless dichloroacetonitrile, b.p. 110–112°/760 mm.,  $n_D^{25}$  1.439,  $d_4^{20}$  1.369. Since this reaction is slightly slower, 30 minutes should be allowed for the reaction before chilling.

### 3. Discussion

Dibromoacetonitrile has been prepared by the dehydration of dibromoacetamide with phosphorous pentoxide<sup>2,3</sup> and by the present method.<sup>4</sup> An early report that dibromoacetonitrile can be obtained from cyanoacetic acid by treatment with bromine,<sup>5</sup> a method similar to that described here, was later shown to be wrong.<sup>2</sup> Dibromoacetonitrile has been prepared also by the bromination of ethyl cyanoacetate in the presence of magnesium oxide.<sup>6</sup>

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### References and Notes

1. Loyola University, Chicago, Illinois.
2. Steinkopf, *Ber.*, **38**, 2694 (1905).
3. Ghigi, *Gazz. chim. ital.*, **71**, 641 (1941).
4. Wilt, *J. Org. Chem.*, **21**, 920 (1956).
5. van't Hoff, *Ber.*, **7**, 1382, 1571 (1874).
6. Felton, *J. Chem. Soc.*, **1955**, 515.

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### Appendix

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

phosphorous pentoxide

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

Ethyl cyanoacetate (105-56-6)

cyanoacetic acid (372-09-8)

Dibromoacetonitrile,  
Acetonitrile, dibromo- (3252-43-5)

N-chlorosuccinimide (128-09-6)

dibromoacetamide

methylene chloride (75-09-2)

Succinimide (123-56-8)

magnesium oxide

N-bromosuccinimide (128-08-5)

dichloroacetonitrile (3018-12-0)