



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.

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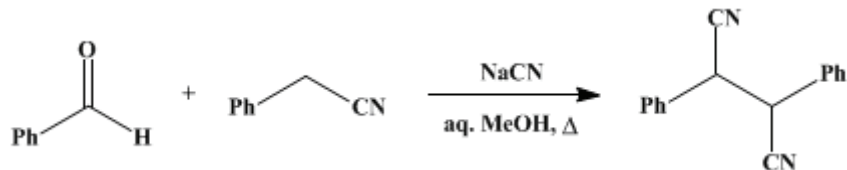
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.392 (1963); Vol. 32, p.63 (1952).*

## 2,3-DIPHENYLSUCCINONITRILE

### [Succinonitrile, 2,3-diphenyl-]

#### [I. METHOD A]



Submitted by R. B. Davis and J. A. Ward, Jr.<sup>1</sup>

Checked by B. C. McKusick and R. L. Morgan.

#### 1. Procedure

*Caution! These operations should be conducted in a good hood.*

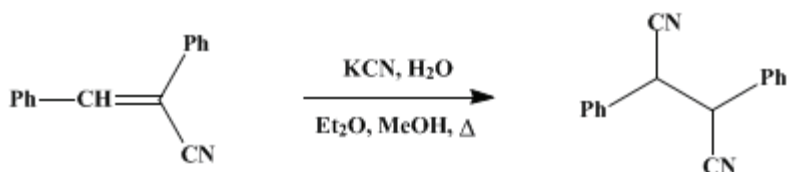
A 1-l. three-necked flask is fitted with a stirrer, a condenser, a dropping funnel, and a heating mantle. Sixty-one grams (1.25 moles) of sodium cyanide and 100 ml. of distilled water are added, and the mixture is warmed with stirring for about 15 minutes while the sodium cyanide dissolves. Then 400 ml. of methanol (Note 1) is introduced, and the mixture is rapidly heated to gentle reflux. Fifty grams (0.42 mole) of benzyl cyanide is added all at once, followed by dropwise addition of a solution of 53 g. (0.50 mole) of benzaldehyde and 30 g. (0.26 mole) of benzyl cyanide (Note 2). The addition requires about 40 minutes, during which time the reaction mixture turns from yellow to green and crystalline 2,3-diphenylsuccinonitrile begins to separate (Note 3). The reaction mixture is stirred at gentle reflux for 30 minutes after the addition is complete. The reaction mixture, now blue in color, becomes brown as it is cooled to room temperature.

The nitrile is separated from the cooled reaction mixture by suction filtration, washed successively with 150-ml. portions of 75% aqueous methanol, water, 75% aqueous methanol, and ether, and dried in air overnight. It is obtained as a colorless solid that weighs 84–89 g. (72–77%) and melts over a range of 1–2° between 202° and 206° (Note 4). It is the *meso*-isomer of 2,3-diphenylsuccinonitrile mixed with a small amount of the *dl*-isomer. Recrystallization from glacial acetic acid (about 27 ml. per g.), followed by washing with 150-ml. portions of water, 75% aqueous methanol, and ether, yields 79–84 g. (68–72%) of the pure *meso*-isomer, m.p. 238–239° (Note 5).

#### 2. Notes

1. Reagent grade methanol, very low in acetone content, is used; that available from Rascher and Betzold or Baker is satisfactory.
2. The benzyl cyanide, chlorine-free benzaldehyde, and reagent grade granular sodium cyanide obtainable from Matheson, Coleman and Bell, are satisfactory.
3. Initial precipitation, occurring during the course of the addition, is exothermic. Hence gentle reflux is advised, and the operator should be prepared to remove the heating mantle for a few minutes should the refluxing become vigorous. Early seeding, if seed is available, is helpful in this regard.
4. Prepared mixtures of the isomeric nitriles have been reported to melt over a range of 1–2° between 206° and 221°.<sup>2</sup>
5. The checkers used a calibrated thermometer and observed a melting point of 229–230° for an analytically pure sample which was heated in an open capillary in an oil bath.

#### [II. METHOD B]



Submitted by J. A. McRae and R. A. B. Bannard<sup>3</sup>.  
 Checked by R. T. Arnold and Stuart W. Fenton.

## 1. Procedure

*Caution! This preparation should be conducted in a good hood.*

Two hundred and five grams (1 mole) of  $\alpha$ -phenylcinnamionitrile,<sup>4</sup> 2250 ml. of methanol, and 750 ml. of ether are placed in a 5-l. round-bottomed flask fitted with a two-necked adapter supporting a 1-l. separatory funnel and reflux condenser. The  $\alpha$ -phenylcinnamionitrile is dissolved by gentle heating, and the solution is heated under reflux. A solution of 274 g. (4 moles) of 95% potassium cyanide in 600 ml. of water (which has been preheated to 45°) is added rapidly from the separatory funnel (Note 1). A small amount of potassium cyanide precipitates. The solution is heated under reflux for 1 hour, after which a solution of 154 g. (2 moles) of ammonium acetate in 250 ml. of water is added rapidly from the separatory funnel (Note 2). Heating is discontinued, and the mixture is allowed to stand for 24 hours. The slightly orange-yellow crystalline product is collected on a Büchner funnel and washed, first with two 300-ml. portions of water at 60° to remove inorganic salts, then with 800 ml. of 70% methanol for removal of water and some unreacted  $\alpha$ -phenylcinnamionitrile, and finally with two 300-ml. portions of ether for further drying. The colorless needles thus obtained consist of a mixture of the stereoisomeric  $\alpha,\alpha'$ -diphenylsuccinonitriles and, after drying at room temperature for 6 hours, weigh 213–218 g. (92–94%). This mixture of stereoisomers melts over a 1–2° range in the region of 202–206° (Note 3).

The mixed dinitrile can be recrystallized from glacial acetic acid (using 27 ml. per g.) to give pure *meso*- $\alpha,\alpha'$ -diphenylsuccinonitrile. Residual acetic acid is removed readily by washing the crystalline product with small portions of water, aqueous methanol (70%), and ether; yield 95–98% (based on mixed dinitrile); m.p. 240–241.5° (cor.).

## 2. Notes

- Care must be exercised to avoid superheating of the solution before addition of the cyanide; otherwise ether and  $\alpha$ -phenylcinnamionitrile will be lost through the condenser. Superheating can be avoided by adding a boiling chip periodically as the solution approaches its boiling point. No difficulty with superheating occurs after the cyanide has been added.
- Addition of the ammonium acetate solution may be omitted; the yield is then 203–208 g. (87.5–89.6%).
- The mixture of dinitriles has been reported to melt over a 1–2° range in the region of 206–221°.<sup>2</sup> Analysis of a sample of the mixture of dinitriles produced by the present method showed that no impurities are present.

## 3. Discussion

A mixture of the stereoisomeric 2,3-diphenylsuccinonitriles has been obtained by the interaction of benzyl cyanide, benzal chloride, and potassium cyanide in aqueous ethanolic solutions;<sup>2</sup> by warming  $\alpha$ -phenylcinnamionitrile with excess potassium cyanide in aqueous ethanolic solution with,<sup>5</sup> or without,<sup>6,7</sup> subsequent addition of dilute acetic acid; by heating under reflux an aqueous ethanolic solution of  $\alpha$ -phenylcinnamionitrile and excess potassium cyanide with subsequent addition of saturated ammonium or magnesium chloride solution;<sup>8</sup> by the action of sunlight on a mixture of benzyl cyanide and benzophenone;<sup>9</sup> and by treatment of benzyl cyanide with sodium methylate and ethereal iodine solution.<sup>10</sup>

In addition, 2,3-diphenylsuccinonitriles have been prepared by treating  $\alpha$ -bromo- or  $\alpha$ -chlorobenzyl cyanide with sodium iodide in acetone solution,<sup>11</sup> and by the condensation of benzyl cyanide, benzaldehyde, and sodium cyanide.<sup>12</sup> The mixture of stereoisomeric 2,3-diphenylsuccinonitriles has been separated into the *meso* compound and the racemic form.<sup>13</sup>

Method I is more practical than Method II, which had been developed earlier, since it affords 2,3-diphenylsuccinonitrile in a single procedure and in good yields from readily available materials.

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## References and Notes

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## Appendix

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

meso- $\alpha,\alpha'$ -diphenylsuccinonitrile

ammonium or magnesium chloride

$\alpha$ -bromo- or  $\alpha$ -chlorobenzyl cyanide

acetic acid (64-19-7)

methanol (67-56-1)

ether (60-29-7)

ammonium acetate (631-61-8)

sodium cyanide (143-33-9)

potassium cyanide (151-50-8)

benzaldehyde (100-52-7)

iodine (7553-56-2)

acetone (67-64-1)

sodium methylate (124-41-4)

Benzophenone (119-61-9)

Benzyl cyanide (140-29-4)

sodium iodide (7681-82-5)

benzal chloride (98-87-3)

$\alpha$ -Phenylcinnamitrile (2510-95-4)

2,3-Diphenylsuccinonitrile,  
Succinonitrile, 2,3-diphenyl- (5424-86-2)