



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.

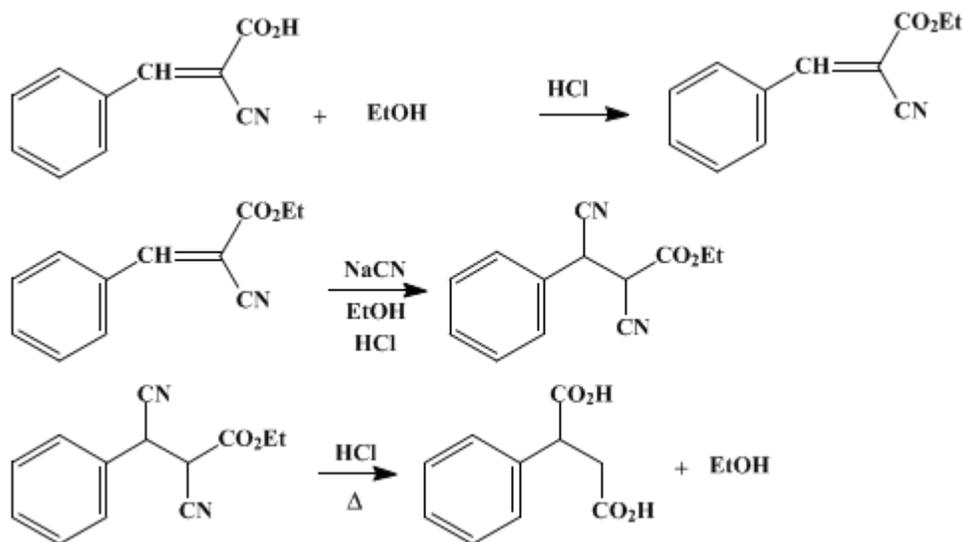
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 1, p.451 (1941); Vol. 8, p.88 (1928).*

## PHENYLSUCCINIC ACID

[Succinic acid, phenyl-]



Submitted by Arthur Lapworth and Wilson Baker.

Checked by J. B. Conant and Mildred Evans.

### 1. Procedure

(A) *Esterification of  $\alpha$ -Cyano- $\beta$ -phenylacrylic Acid.*—In a 200-cc. round-bottomed flask fitted with a reflux condenser, 50 g. (0.29 mole) of dry  $\alpha$ -cyano- $\beta$ -phenylacrylic acid (p. 181) is boiled for four and one-half hours with 100 cc. of absolute alcohol (p. 249) containing 3–4 g. of anhydrous hydrogen chloride (p. 293). The resulting solution is filtered rapidly while hot and allowed to stand overnight. Long, flat, colorless prisms separate which are filtered off with suction, washed with a little cold alcohol, and dried in air. A further small quantity may be obtained by working up the mother liquor. The melting point of the ethyl  $\alpha$ -cyano- $\beta$ -phenylacrylate is 50°, and the yield is 46.5–53 g. (80–91 per cent of the theoretical amount) (Note 1).

(B) *Addition of Sodium Cyanide to Ethyl  $\alpha$ -Cyano- $\beta$ -phenylacrylate.*—Twenty grams (0.1 mole) of cyanophenylacrylic ester is treated with 40 cc. of 50 per cent alcohol and 10 g. (0.2 mole) of finely powdered sodium cyanide. The mixture becomes warm and the ester rapidly dissolves, the reaction being completed by heating on the steam bath for two minutes. To this is added 200 cc. of water, and the resulting clear, colorless solution of the addition product is decomposed with hydrochloric acid. This causes the precipitation of ethyl  $\alpha,\beta$ -dicyano- $\beta$ -phenylpropionate as a yellowish oil, which on standing overnight and being stirred vigorously, or seeded if possible, sets to a yellowish solid mass. This is filtered off with suction and washed with cold water.

(C) *Hydrolysis of Ethyl  $\alpha,\beta$ -Dicyano- $\beta$ -phenylpropionate.*—The product thus obtained is hydrolyzed by boiling under a reflux condenser for four hours with 80 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The substance goes into solution, and this clear solution, on cooling, deposits phenylsuccinic acid in small crystals which are nearly colorless. These are filtered off, washed with cold water, and dried. The yield of product melting at 164–166° is 17.6–18.4 g. (91–95 per cent of the theoretical amount based on the weight of ester used) (Note 2) and (Note 3).

### 2. Notes

1. It is suggested that the esterification may be more conveniently carried out by substituting 95 per cent

for absolute alcohol, and 25 g. concentrated sulfuric acid for the hydrogen chloride, without affecting either the yield or quality of ester (W. E. Barker, private communication).

2. The phenylsuccinic acid, if slightly off color, may be recrystallized easily from a hot water solution by rapid cooling. Five grams is dissolved in 400 cc. of hot water, and then 60 cc. more of hot water is added. This solution is filtered and cooled in ice water with stirring until crystals separate. After standing, the crystals are filtered off. The yield is 4.5 g. (90 per cent) of product melting at 167°.

3. The quantities of material used may be doubled from (B) on, in which case the refluxing in (C) requires at least one-half hour longer for complete solution. One run with double quantities yielded 32.6 g.

### 3. Discussion

Phenylsuccinic acid can be prepared by the action of potassium cyanide and alcohol upon  $\alpha$ -chlorostyrene;<sup>1</sup> by the reaction of ethoxyphenylmaleic anhydride and fuming hydriodic acid at 165°;<sup>2</sup> by the hydrolysis of phenylcyanopropionic acid, obtained by heating ethyl benzalmalonate and aqueous potassium cyanide;<sup>3</sup> by the action of potassium cyanide on ethyl benzalmalonate and saponification of the product with potassium hydroxide;<sup>4</sup> by the hydrolysis with hydrochloric acid of ethyl  $\alpha,\beta$ -dicyano- $\beta$ -phenylpropionate, obtained from sodium ethyl cyanoacetate and mandelonitrile;<sup>5</sup> and by the hydrolysis of the addition product of hydrogen cyanide and ethyl  $\alpha$ -cyano- $\beta$ -phenylacrylate.<sup>6</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 181
- Org. Syn. Coll. Vol. 4, 804

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### References and Notes

1. Rügheimer, Ber. **14**, 428 (1881).
2. Volhard and Henke, Ann. **282**, 83 (1894).
3. Bredt and Kallen, Ann. **293**, 348 (1896).
4. Wegscheider and Hecht, Monatsh. **24**, 417 (1903).
5. Higson and Thorpe, J. Chem. Soc. **89**, 1471 (1906).
6. Lapworth and McRae, J. Chem. Soc. **121**, 1704 (1922); Manske, J. Am. Chem. Soc. **53**, 1106 (1931).

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### Appendix

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

ester

cyanophenylacrylic ester

alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride,  
hydrochloric acid (7647-01-0)

sodium cyanide (143-33-9)

hydrogen cyanide (74-90-8)

potassium cyanide (151-50-8)

potassium hydroxide (1310-58-3)

mandelonitrile (532-28-5)

hydriodic acid (10034-85-2)

$\alpha$ -Cyano- $\beta$ -phenylacrylic acid (1011-92-3)

Phenylsuccinic acid,  
Succinic acid, phenyl- (635-51-8)

$\alpha$ -Chlorostyrene

Ethyl  $\alpha$ -cyano- $\beta$ -phenylacrylate (2025-40-3)

Ethyl  $\alpha,\beta$ -dicyano- $\beta$ -phenylpropionate

ethoxyphenylmaleic anhydride

phenylcyanopropionic acid

Ethyl benzalmalonate

sodium ethyl cyanoacetate