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.

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.

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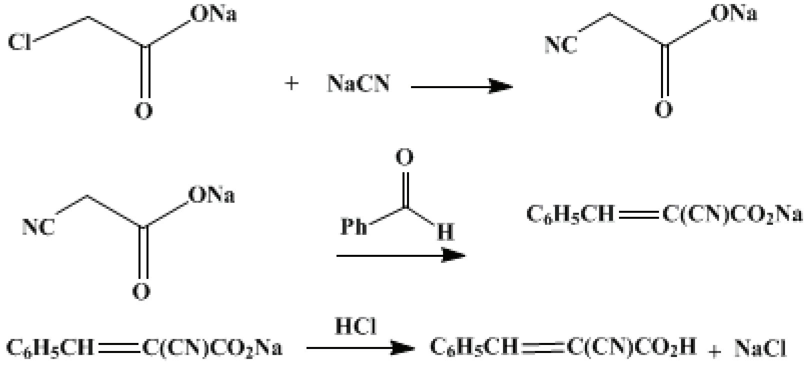
α-CYANO-β-PHENYLACRYLIC ACID



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1. Procedure

(*A*) *Preparation of Sodium Cyanoacetate Solution*.—In a 3-l. round-bottomed flask is placed 250 g. (2.65 moles) of monochloroacetic acid. To this are added 100 cc. of water and 375 g. (1.3 moles) of crystalline sodium carbonate (decahydrate) (Note 1), the mixture being gently warmed. The neutralization is completed by adding sodium carbonate solution using litmus paper as an indicator. The flask is transferred to the hood, and a solution of 130 g. (2.65 moles) of sodium cyanide in 250 cc. of warm water is added in two approximately equal portions, waiting after the first addition until no further evolution of heat occurs, or the mixture ceases to boil. The cooled solution is neutralized with hydrochloric acid, using methyl orange as an outside indicator. The solution is then diluted with water to 1 l. and filtered; it should be of a light straw color. It can be kept for long periods of time in a stoppered bottle, although the color deepens somewhat.

(*B*) *Condensation with Benzaldehyde*.—To 400 cc. (1.06 moles) of the sodium cyanoacetate solution is added a solution of 5 g. (0.13 mole) of sodium hydroxide in 400 cc. of water. The resulting alkaline solution is warmed to 40° and treated with 100 g. (0.94 mole) of benzaldehyde which has been shaken with sodium carbonate solution and distilled under reduced pressure. The benzaldehyde dissolves after vigorous shaking for a few minutes. After standing one hour, during which time some of the sodium cyanophenylacrylate crystallizes (Note 2), the mixture is acidified with concentrated hydrochloric acid until acid to litmus and 40 cc. additional concentrated acid added, and the whole is shaken vigorously. After another hour, the crystalline cyanophenylacrylic acid is filtered on a Büchner funnel, washed thoroughly with cold water, and dried in a steam oven. It is then shaken with 100 cc. of benzene, filtered on a Büchner funnel, and further washed with 50 cc. of benzene and dried. The yield of product melting at 178–179° is 105–115 g. (65–70 per cent of the theoretical amount). This product may have a slight pinkish color, which can be removed by recrystallization from 740 cc. of alcohol or 10 l. of hot water. The recovery is about 57 per cent from alcohol and 92 per cent from water (Note 3). The melting point remains unchanged.

2. Notes

1. In place of the crystallized sodium carbonate, the equivalent amount of dehydrated material (138 g.) and water (240 cc.) may be used.
2. If the sodium salt is crystallized out by chilling externally, then separated and acidified, it gives a purer α-cyano-β-phenylacrylic acid. The yield of acid is 90–105 g., and this purer acid is more satisfactory for the preparation of phenylsuccinic acid (p. 451) (C. F. H. Allen and C. V. Wilson, private communication).
3. Owing to hydrolysis in alkaline or neutral solutions, it is very difficult to free the acid from a slight

odor of benzaldehyde if it is recrystallized from water, but a final washing with benzene removes this odor.

3. Discussion

α-Cyanophenylacrylic acid can be prepared by the hydrolysis of the corresponding ester obtained by the condensation of benzaldehyde with cyanoacetic ester in the presence of sodium alkoxide or acetic anhydride.[1] The direct condensation of benzaldehyde and cyanoacetic acid or its sodium salt takes place when the substances are heated[2] for some time at 180°. The most convenient method for the preparation of the acid (as the sodium or potassium salt) is by the action of benzaldehyde on an alkaline aqueous solution of sodium or potassium cyanoacetate prepared by the interaction of salts of bromoacetic[3] or chloroacetic acids[4] with potassium or sodium cyanide in aqueous solution.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 451

References and Notes

1. Carrick, J. prakt. Chem. (2) **45**, 501 (1892).
2. Fiquet, Ann. chim. phys. (6) **29**, 442 (1893); Bull. soc. chim. (3) **7**, 11 (1892).
3. Clarke and Francis, Ber. **44**, 273 (1911).
4. Lapworth and McRae, J. Chem. Soc. **121**, 1699 (1922).

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

cyanoacetic ester

sodium alkoxide

sodium or potassium cyanoacetate

bromoacetic

chloroacetic acids

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

sodium cyanide (143-33-9)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

monochloroacetic acid (79-11-8)

sodium (13966-32-0)

α-Cyano-β-phenylacrylic acid,
cyanophenylacrylic acid,
α-Cyanophenylacrylic acid (1011-92-3)

Sodium cyanoacetate (1071-36-9)

sodium carbonate (decahydrate) (6132-02-1)

sodium cyanophenylacrylate

Phenylsuccinic acid (635-51-8)

cyanoacetic acid (372-09-8)

potassium (7440-09-7)

sodium salt (824-79-3)