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.

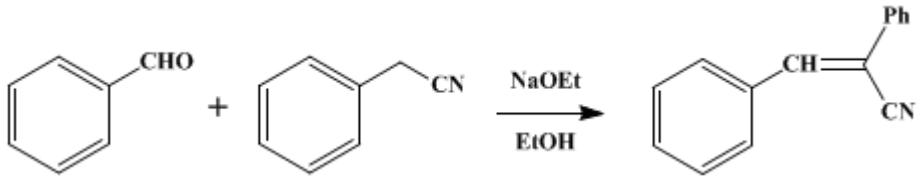
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.029.0083

Organic Syntheses, Coll. Vol. 3, p.715 (1955); Vol. 29, p.83 (1949).

α-PHENYLCINNAMONITRILE

[Acrylonitrile, α-β-diphenyl-]



Submitted by Stanley Wawzonek and Edwin M. Smolin.
Checked by Cliff S. Hamilton and Karl W. R. Johnson.

1. Procedure

In a 2-l. beaker fitted with a strong, efficient, mechanical stirrer is placed a mixture of 106 g. (101 ml., 1 mole) of freshly distilled benzaldehyde and 117 g. (1 mole) of purified dry benzyl cyanide (Note 1), in 650 ml. of 95% ethanol (Note 2). To this mixture is added drop-wise, with stirring, a solution of 7 g. of sodium ethoxide in 50 ml. of absolute ethanol (Note 3). When 40–50 ml. has been added, the mixture becomes warm, turns cloudy, and solidifies. Mechanical stirring is continued as long as possible, and then the mixture is stirred by hand with a thick stirring rod in order to break up the lumps that form. The mixture is cooled in an ice bath (Note 4), and the product is separated by filtration. The filtrate is removed and may be saved (Note 5). The white mass is washed first with 200 ml. of distilled water, then with 50 ml. of 95% ethanol to remove unchanged reagents. The nitrile is dried at 25° and melts at 86–88°. The yield is 178–199 g. (87–97%) of product sufficiently pure for most purposes. Recrystallization from 700 ml. of 95% ethanol gives 170–187 g. (83–91%) of a pure, white product melting at 88° (Note 6).

2. Notes

1. The benzyl cyanide may be purified by a procedure described earlier.[1] If commercial benzyl cyanide is used, the yield is between 80% and 90% of a slightly yellow product. Two recrystallizations are necessary for purification.
2. Denatured alcohol (Formula 3A) containing 10% absolute methanol is a satisfactory solvent for recrystallization.
3. A 40% solution of sodium hydroxide may also be used as the condensing agent; 35–60 ml. is required. With this reagent, the product is less pure and needs an additional recrystallization. The yields range from 70% to 82%.
4. This preliminary cooling helps to prevent clogging of the 20-cm. Büchner funnel used during filtration.
5. An additional 10–21 g. of crude nitrile melting at 84–86° can be obtained by evaporating the combined alcoholic filtrates to a volume of 300 ml. Two or three recrystallizations from 95% ethanol are necessary to raise the melting point to 88°.
6. Similar yields of substituted α-phenylcinnamonitriles can be obtained using *p*-methoxybenzyl cyanide and anisaldehyde, or benzyl cyanide and anisaldehyde.[2,3]

3. Discussion

α-Phenylcinnamonitrile can be prepared from benzaldehyde and benzyl cyanide with no solvent and with sodium ethoxide as a catalyst.[4] Sodium hydroxide[5] (40%) or piperidine[6] may also be used as catalysts. The nitrile has been made by the condensation of benzyl cyanide and excess benzyl chloride with strong sodium hydroxide at 170°[7,8] and by heating α,β-diphenylsuccinonitrile with alcohol at 180° in a sealed tube[9] or at 230–250° under 100–110 mm. pressure with palladium.[10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 392

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 108 (1941).
2. Wawzonek, *J. Am. Chem. Soc.*, **68**, 1157 (1946).
3. Niederl and Ziering, *J. Am. Chem. Soc.*, **64**, 885 (1942).
4. De Schuttenbach, *Ann. chim.*, (11) **6**, 90 (1936).
5. Walther, *J. prakt. Chem.*, (2) **53**, 454 (1896).
6. Knoevenagel, Ger. pat. 94,132 [*Chem. Zentr.*, **69**, 228 (1898)].
7. Neure, *Ann.*, **250**, 155 (1888).
8. Janssen, *Ann.*, **250**, 129 (1888).
9. Chalaney and Knoevenagel, *Ber.*, **25**, 297 (1892).
10. Knoevenagel and Bergdott, *Ber.*, **36**, 2861 (1903).

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

ethanol (64-17-5)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

benzaldehyde (100-52-7)

piperidine (110-89-4)

sodium ethoxide (141-52-6)

palladium (7440-05-3)

benzyl chloride (100-44-7)

Benzyl cyanide (140-29-4)

α-Phenylcinnamonitrile,
Acrylonitrile, α-β-diphenyl- (2510-95-4)

α,β-diphenylsuccinonitrile (5424-86-2)

anisaldehyde (123-11-5)

p-methoxybenzyl cyanide (104-47-2)