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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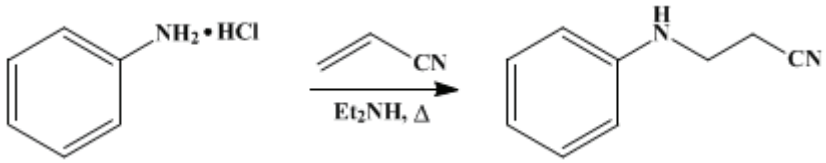
N-2-CYANOETHYLANILINE

[Propionitrile, 3-anilino-]



Submitted by J. Cymerman-Craig and M. Moyle[1].
Checked by William S. Johnson and Duff S. Allen, Jr..

1. Procedure

A mixture of 12.95 g. (0.10 mole) of aniline hydrochloride (Note 1), 6.6 g. (0.12 mole) of acrylonitrile, and 9.1 g. (0.12 mole) of diethylamine (Note 2) is placed in a 100-ml. round-bottomed flask fitted with an efficient reflux condenser and heated for 2.5 hours in a bath maintained at 180°.

The melt is cooled to 0°, 50 ml. of 10% aqueous sodium hydroxide solution is added, and the mixture is extracted with four 50-ml. portions of chloroform. The combined chloroform extracts are washed with two 25-ml. portions of water, and these in turn are extracted with 10 ml. of chloroform. The organic layers are combined and dried partially over anhydrous sodium sulfate. The solvent is removed by distillation on the steam bath, and the residue is distilled at reduced pressure from a 50-ml. distilling flask. After a fore-run of about 4 g. (Note 3), b.p. 60–70°/1.5 mm. (bath temperature taken up to 125°), the cyanoethylaniline is collected at 115–120°/0.01 mm. The product solidifies in the form of colorless plates, m.p. 48–51° (Note 4). The yield is 10.5–11.4 g. (72–78%) (Note 5).

2. Notes

1. An equimolar quantity of aniline benzenesulfonate may be used in place of the hydrochloride.
2. No reaction occurs if the diethylamine is omitted.
3. In a typical run this fraction weighed 4.4 g. and contained 1.6 g. of aniline (estimated as acetanilide) and 2.8 g. of 3-diethylaminopropionitrile.
4. Reported properties are b.p. 178–186°/16 mm. and m.p. 51.5°.[2]
5. The submitters have found that other arylamines may be employed in a similar manner in place of aniline. Thus N-2-cyanoethyl-*p*-anisidine was obtained in 76% yield as plates, m.p. 62–64°, b.p. 130–140°/0.01 mm.; N-2-cyanoethyl-*m*-chloroaniline, in 42% yield as needles, m.p. 44–46°, b.p. 125–130°/0.01 mm.; N,N'-bis-2-cyanoethyl-*o*-phenylenediamine, in 70% yield as needles, m.p. 116–118°, b.p. 190–200°/0.01 mm.; and N,N'-bis-2-cyanoethyl-*p*-phenylenediamine in 22% yield as plates, m.p. 138–139°.

3. Discussion

N-2-Cyanoethylaniline has been prepared (accompanied by much of the N,N'-bis-2-cyanoethyl compound) by heating aniline, acrylonitrile, and acetic acid in an autoclave,[2,3] or at refluxing temperature for 10 hours in the presence of various inorganic catalysts.[4] The substance also has been obtained, free of the N,N'-bis-2-cyanoethyl compound from aniline salts and β-diethylaminopropionitrile.[5,6,7] A number of other cyanoethylated compounds have been heated with aniline and water to form N-2-cyanoethylaniline,[8] and a study has been made of the conditions for the addition of aromatic amines to acrylonitrile.[9]

Heininger[10] has shown that cupric acetate is a superior catalyst for the cyanoethylation of aniline; N-2-cyanoethylaniline has been obtained in 73% yield by this method. The use of cupric acetate as a catalyst in cyanoethylation is demonstrated in the procedure for the preparation of 3-(*o*-chloroanilino)

propionitrile (p. 146).

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 146

References and Notes

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

acetic acid (64-19-7)

aniline (62-53-3)

Acetanilide (103-84-4)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

aniline hydrochloride (142-04-1)

cupric acetate (142-71-2)

diethylamine (109-89-7)

acrylonitrile (107-13-1)

3-diethylaminopropionitrile,
β-diethylaminopropionitrile (5351-04-2)

N-2-Cyanoethylaniline,
Propionitrile, 3-anilino-,
cyanoethylaniline (1075-76-9)

aniline benzenesulfonate

3-(o-chloroanilino) propionitrile (94-89-3)

N-2-cyanoethyl-p-anisidine

N-2-cyanoethyl-m-chloroaniline

N,N'-bis-2-cyanoethyl-o-phenylenediamine

N,N'-bis-2-cyanoethyl-p-phenylenediamine