



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.

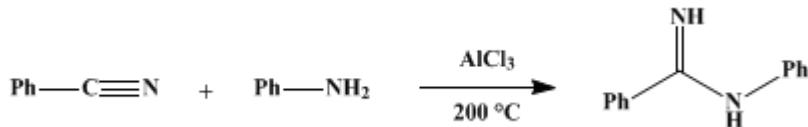
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 4, p.769 (1963); Vol. 36, p.64 (1956).

N-PHENYLBENZAMIDINE

[Benzamidine, N-phenyl-]



Submitted by F. C. Cooper and M. W. Partridge¹.

Checked by T. L. Cairns, R. E. Benson, and V. J. Webers.

1. Procedure

Sixty-two grams (61 ml., 0.67 mole) of aniline (Note 1) is mixed with 68.5 g. (0.66 mole) of benzonitrile in a 250-ml., wide-mouthed flask, and, during about 20 minutes, 89 g. (0.67 mole, calculated as AlCl_3) of a freshly opened sample of powdered, anhydrous aluminum chloride is added in portions with thorough stirring (Note 2). The mixture is then heated at 200° for 30 minutes (Note 3), and, while still molten, is poured slowly into a thoroughly stirred mixture of 20 ml. of concentrated hydrochloric acid and 1.6 l. of water. After the addition of 20 g. of activated carbon, the suspension is stirred while being externally cooled in running water and is then filtered through a kieselguhr filter (Note 4). The filtrate is poured in a steady stream into a stirred solution of 220 g. of sodium hydroxide in 1.2 l. of water. The flocculent precipitate is collected on alkali-resistant paper in a 12-cm. Büchner funnel with the aid of suction, washed with water (Note 5), broken up thoroughly, and air-dried at room temperature to constant weight. The yield of white product, m.p. $111\text{--}115^\circ$, is 90–96 g. (69–74%). This material is sufficiently pure for most purposes. Recrystallization from benzene (60 ml. per 10 g. of amidine) yields 56–74 g. of white powder; concentration of the mother liquors raises the total yield of N-phenylbenzimidine to 69–86 g. (53–66%), melting at $114\text{--}115.5^\circ$.

2. Notes

1. It is preferable to use aniline freshly redistilled from a small quantity of zinc dust.
2. The reaction is strongly exothermic. Although loss of reagents by volatilization is small, it is advisable to close the flask with a loose plug of cotton wool.
3. Below about 180° the mixture is too stiff to be stirred, but at 200° it is a mobile liquid.
4. A suitable filter is prepared by distributing a slurry of 10–15 g. of "Super-Cel" in water on a filter paper in a 12-cm. Büchner funnel and washing with water with the aid of suction until a clear filtrate is obtained.
5. Washing is best effected by vigorously stirring the cake with water until it is completely dispersed, collecting again, and draining well; three such washings are usually sufficient.

3. Discussion

This method is based on the procedure of Oxley, Partridge, and Short.² N-Phenylbenzimidine has also been prepared by heating aniline hydrochloride with benzonitrile or thiobenzamide³ or by heating aniline benzenesulfonate with benzonitrile;⁴ by the action of sodium or sodamide on a mixture of aniline and benzonitrile;⁵ by treating phenylcyanamide with phenylmagnesium bromide;⁶ by the interaction of aniline and benziminoethyl ether hydrochloride;⁷ by the reaction between N-phenylbenzimidyl chloride and ammonia;⁸ by the action of sodamide on benzylidene aniline;^{7,9} by hydrogenating benzanimide oxime;¹⁰ by treating benzophenone oxime benzenesulfonate with ammonia;¹¹ and by the reaction of 2-nitrobutyl benzimidate hydrochloride with aniline.¹²

References and Notes

1. The University, Nottingham, England.
 2. Oxley, Partridge, and Short, *J. Chem. Soc.*, **1947**, 1112; Short and Partridge (Boots Pure Drug Company), Brit. pat. 598,453 [*C. A.*, **42**, 6854 (1948)]; U. S. pat. 2,450,386 [*C. A.*, **43**, 3456 (1949)].
 3. Bernthsen, *Ann.*, **184**, 348 (1877).
 4. Oxley and Short, *J. Chem. Soc.*, **1946**, 147.
 5. Lottermoser, *J. prakt. Chem.*, **54**, 116 (1896); Cooper and Partridge, *J. Chem. Soc.*, **1953**, 255.
 6. Busch and Hobein, *Ber.*, **40**, 4298 (1907).
 7. Lossen and Kobbert, *Ann.*, **265**, 138 (1891); Sugasawa and Ohara, *J. Pharm. Soc. Japan*, **72**, 1036 (1952) [*C. A.*, **47**, 7461 (1953)].
 8. Ghadiali and Shah, *J. Univ. Bombay*, **6**, 127 (1937) [*C. A.*, **32**, 3761 (1938)].
 9. Kirssanow and Iwastchenko, *Bull. soc. chim. France*, [5] **2**, 2118 (1935).
 10. Barber and Self (May and Baker Ltd.), U. S. pat. 2,375,611 [*C. A.*, **39**, 3544 (1945)].
 11. Oxley and Short, *J. Chem. Soc.*, **1948**, 1519.
 12. Cooper and Partridge, *J. Chem. Soc.*, **1952**, 5036.
-

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

N-phenylbenzimidyl chloride

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

aniline (62-53-3)

benzonitrile (100-47-0)

sodium hydroxide (1310-73-2)

aniline hydrochloride (142-04-1)

benzylidene aniline (538-51-2)

carbon (7782-42-5)

aluminum chloride (3495-54-3)

zinc (7440-66-6)

sodium (13966-32-0)

Phenylmagnesium bromide (100-58-3)

sodamide (7782-92-5)

thiobenzamide (2227-79-4)

phenylcyanamide

aniline benzenesulfonate

N-Phenylbenzamidine,
Benzamidine, N-phenyl- (1527-91-9)

benziminoethyl ether hydrochloride

benzanilide oxime

benzophenone oxime benzenesulfonate

2-nitrobutyl benzimidate hydrochloride

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved