



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.

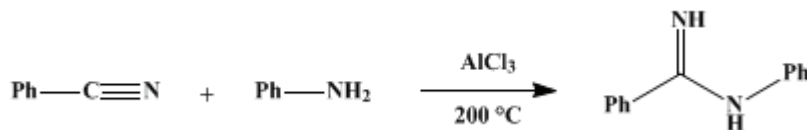
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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N-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. 111–115°, 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-phenylbenzamidine](#) to 69–86 g. (53–66%), melting at 114–115.5°.

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-Phenylbenzamidine](#) has also been prepared by heating [aniline hydrochloride](#) with [benzonitrile](#) or [thiobenzamide](#)³ 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 [benziminioethyl 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 [benzanilide 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)].
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 5. Lottermoser, *J. prakt. Chem.*, **54**, 116 (1896); Cooper and Partridge, *J. Chem. Soc.*, **1953**, 255.
 6. Busch and Hobein, *Ber.*, **40**, 4298 (1907).
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 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.
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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)

benzotrile (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)

benzimidinoethyl ether hydrochloride

benzanilide oxime

benzophenone oxime benzenesulfonate

2-nitrobutyl benzimidate hydrochloride