



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.

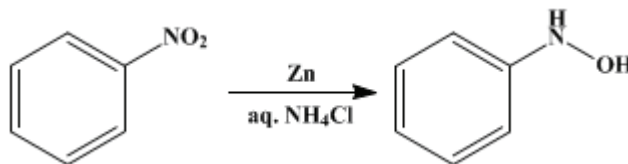
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.445 (1941); Vol. 4, p.57 (1925).

β-PHENYLHYDROXYLAMINE

[Hydroxylamine, N-phenyl-]



Submitted by Oliver Kamm
Checked by C. S. Marvel

1. Procedure

In a 16-l. earthenware jar are placed 250 g. (4.7 moles) of technical [ammonium chloride](#), 8 l. of water, and 500 g. (416 cc., 4.1 moles) of [nitrobenzene](#). The mixture is stirred vigorously by means of a mechanical stirrer, and 620 g. (8.1 atoms) of [zinc](#) dust of 85 per cent purity is added ([Note 1](#)) during the course of fifteen to twenty minutes ([Note 2](#)). As the reduction proceeds, the temperature rises to 60–65°. Stirring is continued for fifteen minutes after all the [zinc](#) dust has been added, at the end of which time the reaction is complete, as indicated by the fact that the temperature of the mixture ceases to rise.

While still hot, the solution is filtered with suction in order to remove the [zinc oxide](#), which is washed with 1 l. of hot water. The filtrate is placed in an enameled pan, saturated with salt, about 3 kg. being required, and cooled to 0° by being placed in an ice-salt mixture. The [phenylhydroxylamine](#), which crystallizes out in long, light yellow needles ([Note 3](#)), is filtered by suction. The yield of crude product varies considerably, depending upon the amount of salt solution present, but averages 350–400 g. This corresponds to 275–300 g. (62–68 per cent of the theoretical amount) of actual [phenylhydroxylamine](#), as determined by its separation from inorganic materials by solution in [ether](#) ([Note 4](#)).

Since [phenylhydroxylamine](#) deteriorates upon storage, it is generally used promptly, as illustrated in the preparation of [cupferron](#) (p. 177). The oxalate is somewhat more stable.

2. Notes

1. The [zinc](#) dust must be analyzed (Gattermann, "Practical Methods of Organic Chemistry," 3rd ed., p. 390), and a proportional quantity used if the [zinc](#) content is not 85 per cent. Technical [nitrobenzene](#) is satisfactory if it distills over a range of not more than 5° and is not acid in reaction.
2. When the reaction is run more slowly, the temperature does not reach 60–65° and the yield is poorer. At 50–55°, the yield is about 55 per cent.
3. It is important that the [phenylhydroxylamine](#) solution be kept at 0° for at least one-half hour or considerable material will be lost in the solution. The use of an enameled pail saves a great deal of time at this step.
4. [Phenylhydroxylamine](#) is soluble in saturated salt solution at 0° to the extent of about 9 g. per liter, but this amount is not included in the yields given. Occasional yields of 300–310 g. of dry [phenylhydroxylamine](#) have been obtained.

3. Discussion

β-Phenylhydroxylamine can be prepared by the reduction of [nitrobenzene](#) by [zinc](#) dust,¹ a method in which various solvents and catalysts have been used, and in which copper-coated and amalgamated zinc, as well as [aluminum](#) amalgam,² have been substituted for the [zinc](#) dust; by ammonium sulfide;³ by sodium in liquid ammonia;⁴ and by the oxidation of [anilinomagnesium bromide](#) with an [ether](#) solution of [hydrogen peroxide](#).⁵ The procedure described is like an earlier method,⁶ but it has been found⁷ that

cooling is not essential. The preparation of the oxalate has been described.⁸

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 177](#)
- [Org. Syn. Coll. Vol. 5, 957](#)
- [Org. Syn. Coll. Vol. 5, 1124](#)
- [Org. Syn. Coll. Vol. 8, 16](#)

References and Notes

1. Bamberger, Ber. **27**, 1348, 1548 (1884); Wohl, Ber. **27**, 1432 (1894).
2. Wislicenus, Ber. **29**, 494 (1896); Lapworth and Pearson, J. Chem. Soc. **119**, 767 (1921); Kasanof, J. Ind. Eng. Chem. **12**, 799 (1920).
3. Willstätter and Kubli, Ber. **41**, 1936 (1908); Slotta and Jacobi, Z. anal. Chem. **80**, 97 (1930).
4. White and Knight, J. Am. Chem. Soc. **45**, 1784 (1923).
5. Oddo and Binaghi, Gazz. chim. ital. **54**, 193 (1924); Atti accad. Lincei **32**, II, 349 (1923) [C. A. **18**, 3166 (1924)]; Durand and Naves, Compt. rend. **180**, 521 (1925).
6. Kalle and Co., Ger. pat. 89,978 [Frdl. **4**, 47 (1894-97)].
7. Marvel and Kamm, J. Am. Chem. Soc. **41**, 277 (1919).
8. Sulzberger, U. S. pat. 1,390,260 [C. A. **16**, 105 (1922)].

Appendix

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

β -Phenylhydroxylamine

copper-coated and amalgamated zinc

ammonium sulfide

sodium in liquid ammonia

[ether \(60-29-7\)](#)

[ammonium chloride \(12125-02-9\)](#)

[aluminum \(7429-90-5\)](#)

[zinc \(7440-66-6\)](#)

[Nitrobenzene \(98-95-3\)](#)

[hydrogen peroxide \(7722-84-1\)](#)

[Cupferron \(135-20-6\)](#)

[Phenylhydroxylamine,](#)

Hydroxylamine, N-phenyl- (100-65-2)

zinc oxide

anilinomagnesium bromide

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