



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.

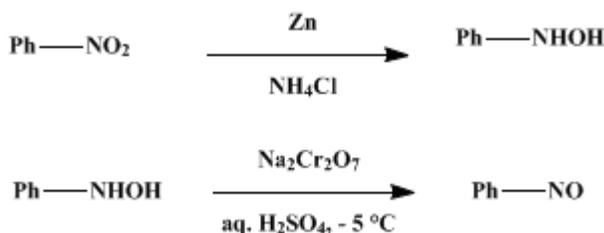
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.668 (1955); Vol. 25, p.80 (1945).

NITROSOBENZENE

[Benzene, nitroso-]



Submitted by George H. Coleman, Chester M. McCloskey, and Frank A. Stuart.
Checked by W. E. Bachmann, N. C. Deno, and R. F. Edgerton.

1. Procedure

A mixture of 250 ml. (2.44 moles) of [nitrobenzene](#) ([Note 1](#)) and ([Note 2](#)) and a solution of 150 g. of [ammonium chloride](#) in 5 l. of water in a 5-gal. crock ([Note 3](#)) is stirred vigorously ([Note 4](#)), and 372 g. (5.15 moles) of [zinc](#) dust (90% [zinc](#)) is added in small portions over a period of 5 minutes. About 5 minutes after the addition of the [zinc](#), the main reaction occurs and the temperature rises. When the temperature reaches about 65°, enough ice is added to the stirred mixture to bring the temperature down to 50–55° ([Note 5](#)). Twenty minutes after the addition of [zinc](#) was started, the solution is filtered through a 24-cm. Büchner funnel and the [zinc oxide](#) residues are washed with 3 l. of boiling water. The filtrate and washings are combined in a 6-gal. crock ([Note 6](#)) and cooled immediately ([Note 7](#)) by the addition of enough ice to bring the temperature to 0° to –2° and leave at least 1 kg. of ice unmelted.

To this cold solution or suspension of β -phenylhydroxylamine, a cold solution of [sulfuric acid](#) (750 ml. of concentrated acid and sufficient ice to bring the temperature down to –5°) is added with stirring. An ice-cold solution of 170 g. of [sodium dichromate dihydrate](#) in 500–750 ml. of water is added as rapidly as it can be poured into the mixture, which is stirred or swirled ([Note 8](#)). After 2 to 3 minutes, the straw-colored precipitate of [nitrosobenzene](#) is collected on a Büchner funnel and washed with 1 l. of water ([Note 9](#)).

The crude [nitrosobenzene](#) is steam-distilled ([Note 10](#)), and the distillate is collected in a receiver cooled by ice ([Note 11](#)). The [nitrosobenzene](#) is finely ground in a mortar, transferred to a Büchner funnel, and washed with water until the washings are no longer brown. After it has been sucked as dry as possible on the filter the [nitrosobenzene](#) is pressed between layers of filter paper (or other porous paper). One or two changes of paper may be necessary. The yield of [nitrosobenzene](#) melting at 64–67° is 128–138 g. (49–53%) ([Note 12](#)) and ([Note 13](#)). If a purer product is desired, the crude [nitrosobenzene](#) can be recrystallized from a small amount of [ethanol](#) with good cooling, and the product dried over [calcium chloride](#) at atmospheric pressure.

2. Notes

- Commercial [nitrobenzene](#) of good quality is satisfactory.
- Contact with [nitrobenzene](#), [phenylhydroxylamine](#), and [nitrosobenzene](#) or prolonged breathing of the vapors should be avoided.
- The checkers used a 12-l. round-bottomed flask.
- Vigorous stirring is necessary in order to prevent the [zinc](#) dust from caking on the bottom of the crock. The submitters employed two mechanically driven stirrers in order to keep the [zinc](#) dust in suspension. The checkers used a single paddle stirrer successfully.
- At higher temperatures secondary reactions take place.
- The checkers used a 22-l. round-bottomed flask.
- Since β -phenylhydroxylamine decomposes on standing, the filtrate should be cooled as soon as the

filtration is completed, and the oxidation to [nitrosobenzene](#) should be carried out immediately. An excess of ice should be present since the oxidation reaction is exothermic and the temperature of the solution should still be near 0° after the oxidation. At higher temperatures oxidation products other than [nitrosobenzene](#) are produced.

8. It is important to add the dichromate solution rapidly in order to obtain a good yield of easily filterable product. In a run in which the dichromate solution was added over a period of 25 minutes, only a 10% yield of [nitrosobenzene](#) was obtained.

9. This product is stable for about a week if kept at 0°.

10. Connections should be of glass since cork and rubber are attacked readily. Since [nitrosobenzene](#) decomposes at the elevated temperature, it should be steam-distilled as rapidly as possible. If several runs are made, not more than four or five should be combined for distillation. A Hopkins still head is effective for preventing contamination.

The [nitrosobenzene](#) condenses to a green liquid which solidifies to a white solid. Care should be taken that the solid does not clog the condenser. Distillation is stopped when yellow oily material appears in the condenser.

11. Cooling of the receiver is necessary because the [nitrosobenzene](#) has a very high vapor pressure at room temperature.

12. Yields as high as 65–70% have been obtained in smaller runs.

13. [Nitrosobenzene](#) can be kept at room temperature in a closed container for 1–2 days. Over longer periods it should be stored at 0°.

3. Discussion

[Nitrosobenzene](#) can be prepared by the oxidation of [aniline](#) with permonosulfuric acid¹ or [peracetic acid](#)² and by the oxidation of β -phenylhydroxylamine,³ which is prepared by the reduction of [nitrobenzene](#). Purification by sublimation has been recommended.⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 711](#)

References and Notes

1. Caro, *Z. angew. Chem.*, **11**, 845 (1898).
2. D'Ans and Kneip, *Ber.*, **48**, 1144 (1915).
3. Bamberger, *Ber.*, **27**, 1555 (1894); Parsons and Bailar, *J. Am. Chem. Soc.*, **58**, 268 (1936).
4. Robertson and Vaughan, *J. Chem. Education*, **27**, 605 (1950).

Appendix

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

β -Phenylhydroxylamine

[ethanol](#) (64-17-5)

[calcium chloride](#) (10043-52-4)

[sulfuric acid](#) (7664-93-9)

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

[aniline \(62-53-3\)](#)

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

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

[Phenylhydroxylamine \(100-65-2\)](#)

[zinc oxide](#)

[sodium dichromate dihydrate \(10588-01-9\)](#)

[peracetic acid \(79-21-0\)](#)

[Nitrosobenzene,
Benzene, nitroso- \(586-96-9\)](#)