



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](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.

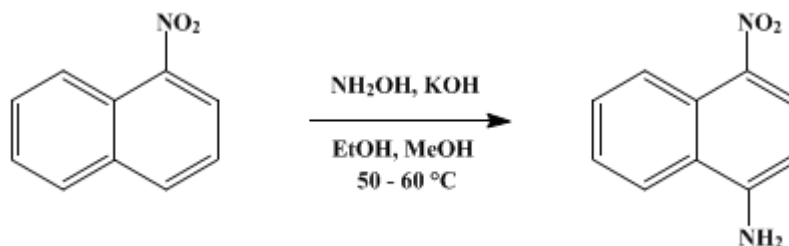
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.664 (1955); Vol. 28, p.80 (1948).*

## 4-NITRO-1-NAPHTHYLAMINE

### [1-Naphthylamine, 4-nitro-]



Submitted by Charles C. Price and Sing-Tuh Voong.  
Checked by Richard T. Arnold and Jay S. Buckley, Jr..

### 1. Procedure

Twenty grams (0.115 mole) of  $\alpha$ -nitronaphthalene (Note 1) and 50 g. (0.72 mole) of powdered hydroxylamine hydrochloride are dissolved in 1.2 l. of 95% ethanol contained in a 3-l. flask which is heated in a bath maintained at 50–60°. A filtered solution of 100 g. of potassium hydroxide in 500 g. (630 ml.) of methanol is added gradually with vigorous mechanical stirring (Note 2) over a period of 1 hour. Stirring is continued for an additional hour, and the warm solution is poured slowly into 7 l. of ice water. After the solid has coagulated, it is collected on a filter and washed thoroughly with water. The crude 4-nitro-1-naphthylamine is purified by recrystallization from 500 ml. of 95% ethanol (Note 3). About 12–13 g. (55–60%) of long golden-orange needles, m.p. 190.5–191.5°, is obtained.

### 2. Notes

1. The  $\alpha$ -nitronaphthalene, m.p. 56–57°, was obtained from Eastman Kodak Company.
2. The color changes from yellow to orange, and potassium chloride separates.
3. In some experiments a few milliliters of dilute hydrochloric acid (1:1) or sulfuric acid (1:1) was added to facilitate the crystallization of the 4-nitro-1-naphthylamine.

### 3. Discussion

This method is essentially that described by Goldhahn.<sup>1</sup> 4-Nitro-1-naphthylamine has also been prepared by the nitration of  $\alpha$ -naphthylamine,<sup>2</sup> acetyl- $\alpha$ -naphthylamine,<sup>3,4</sup> and ethyl-1-naphthyloxamate,<sup>5,6</sup> by the oxidation of 4-nitroso-1-naphthylamine,<sup>7</sup> and by reaction of 4-chloro-1-nitronaphthalene with ammonia.<sup>8</sup>

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 341*

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### References and Notes

1. Goldhahn, *J. prakt. Chem.*, **156**, 315 (1940); **157**, 96 (1940).
2. Meldola and Streatfeild, *J. Chem. Soc.*, **63**, 1055 (1893).
3. Lellmann and Remy, *Ber.*, **19**, 796 (1886).
4. Hodgson and Walker, *J. Chem. Soc.*, **1933**, 1205.
5. Lange, Ger. pat. 58,227 [*Frld.*, **3**, 509 (1890–1894)].
6. Sergievskaya, Russ. pat. 50,696 (1937); *J. Gen. Chem. U.S.S.R.*, **10**, 55 (1940)

7. Vorozhtsov and Kozlov, *J. Gen. Chem. U.S.S.R.*, **9**, 587 (1939).  
8. Ger. pat. 117,006 [*Frdl.*, **6**, 176 (1900–1902)].
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

$\alpha$ -naphthylamine

acetyl- $\alpha$ -naphthylamine

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

potassium hydroxide (1310-58-3)

Hydroxylamine hydrochloride (5470-11-1)

$\alpha$ -nitronaphthalene (86-57-7)

potassium chloride (7447-40-7)

4-nitro-1-naphthylamine,  
1-Naphthylamine, 4-nitro- (776-34-1)

ethyl-1-naphthyloxamate

4-nitroso-1-naphthylamine

4-chloro-1-nitronaphthalene