



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.

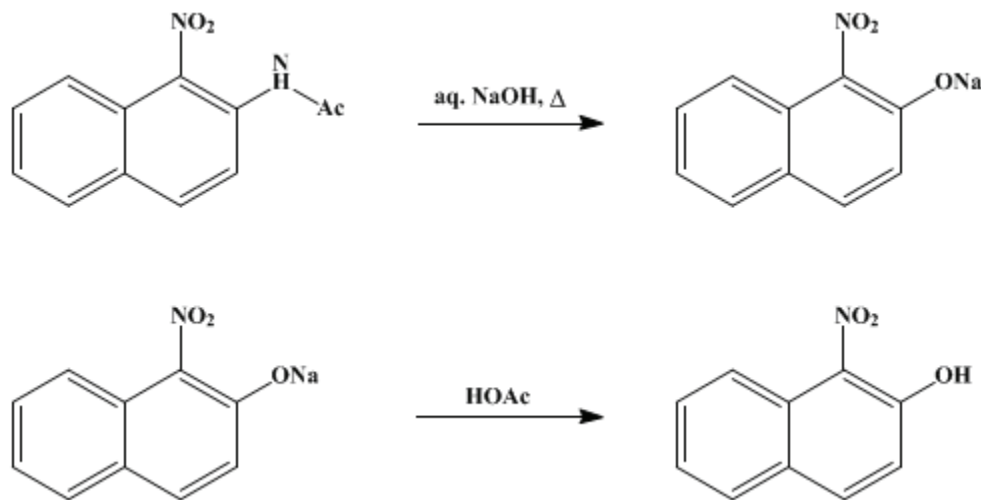
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1-NITRO-2-NAPHTHOL

[2-Naphthol, 1-nitro-]



Submitted by W. W. Hartman, J. R. Byers, and J. B. Dickey.
Checked by Louis F. Fieser and J. T. Walker.

1. Procedure

In a 3-l. round-bottomed flask, fitted with a reflux condenser, are placed 100 g. (0.435 mole) of 1-nitro-2-acetylnaphthalene (p. 438) and a solution of 112 g. (2.8 moles) of sodium hydroxide in 2.7 l. of water (Note 1). The mixture is boiled until ammonia is no longer evolved (six to seven hours). The solution becomes deep red in color. It contains suspended crystals of sodium nitronaphthoxide; these are dissolved by the addition of 1 l. of hot water. The small amount of insoluble material is removed by filtration, washed with hot water until the washings are colorless, and then discarded although it contains a little nitronaphthylamine. The combined washings and filtrate are made acid by adding 500 cc. of glacial acetic acid. The nitronaphthol precipitates as small, bright yellow crystals which are filtered on a 10-cm. Büchner funnel, washed with water, and dried. The yield of material melting at 101–103° is 76–81 g. (92–98 per cent of the theoretical amount).

The product is purified by recrystallization from 500 cc. of methyl alcohol containing 5 cc. of concentrated hydrochloric acid. The first crop of crystals amounts to 60 g. and melts at 103–104°. The mother liquors are concentrated to 150 cc., and a second crop weighing 12–13 g. is collected. The total yield of recrystallized material is 72–73 g. (88–89 per cent of the theoretical amount).

2. Notes

1. This concentration of alkali was found to be very satisfactory. The hydrolysis takes place rather rapidly at first when stronger alkali is used, with the precipitation of the sodium salt which forms a thick paste and causes bumping. When more dilute alkali is used, much more time is required to complete the hydrolysis.

3. Discussion

1-Nitro-2-naphthol has been prepared by the nitration of β -naphthyl ethyl ether;^{1, 2} by the oxidation of 1-nitroso-2-naphthol;³ and by the treatment of β -naphthol with diacetylnitric acid.⁴ It has also been prepared by the treatment of β -naphthylamine with three moles of sodium nitrite in the presence of an excess of acid;⁵ by the decomposition of benzeneazo- β -naphthol with nitric acid;⁶ by heating the nitrate of pseudocumeneazo- β -naphthol under reduced pressure;⁶ by the treatment of 1-bromo-2-naphthol in

acetic acid with nitric acid;⁷ and by the reaction of nitrogen dioxide with β -naphthol.⁷ It has been prepared from 1-nitro-1-bromo-2-ketodihydronaphthalene by treatment with caustic alkali,⁸ and by the fusion of α -nitronaphthalene with sodium hydroxide.⁹

The method on which this procedure is based has been described by Andreoni and Biedermann and by others.¹⁰

References and Notes

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Appendix

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

diacetylnitric acid

sodium nitronaphthoxide

nitrate of pseudocumeneazo- β -naphthol

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

sodium nitrite (7632-00-0)

β -naphthol (135-19-3)

nitrogen dioxide (10102-44-0)

α -nitronaphthalene (86-57-7)
1-nitroso-2-naphthol (131-91-9)
1-Nitro-2-acetylamino-naphthalene (5419-82-9)
1-Nitro-2-naphthol,
2-Naphthol, 1-nitro- (550-60-7)
nitronaphthylamine
nitronaphthol (607-24-9)
 β -naphthyl ethyl ether (93-18-5)
benzeneazo- β -naphthol
1-bromo-2-naphthol (573-97-7)
1-nitro-1-bromo-2-ketodihydronaphthalene
 β -naphthylamine (91-59-8)