Organic Syntheses

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.

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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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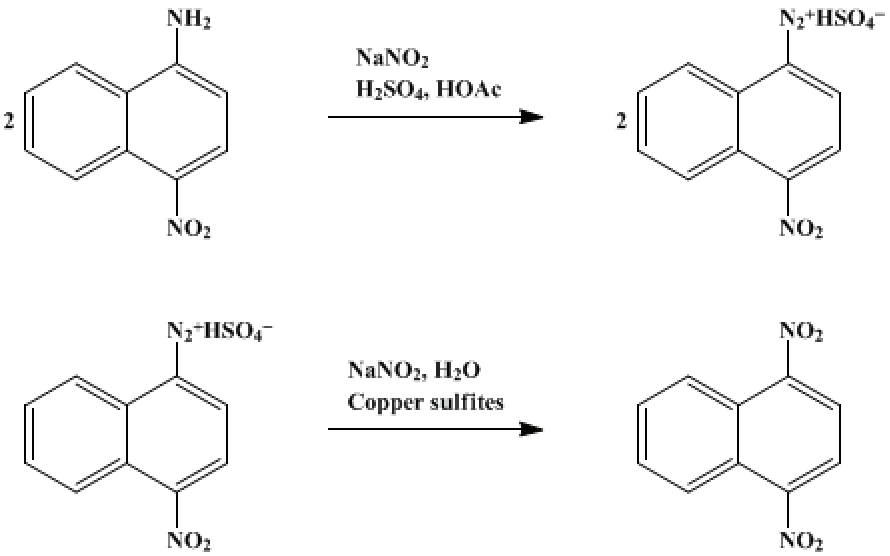
# 1,4-DINITRONAPHTHALENE

## [Naphthalene, 1,4-dinitro-]



Submitted by H. H. Hodgson, A. P. Mahadevan, and E. R. Ward.
Checked by C. C. Price and Sing-Tuh Voong.

## 1. Procedure

Ten grams (0.14 mole) of powdered sodium nitrite is dissolved in 50 ml. of concentrated sulfuric acid (sp. gr. 1.84) contained in a 1-l. beaker placed in an ice bath. A solution of 10 g. of 4-nitro-1-naphthylamine (0.053 mole) (p. 664) in 100 ml. of glacial acetic acid is prepared by heating, and the well-stirred solution is cooled below 20°. Some crystals separate. The resulting thin slurry is dropped slowly into the cold solution of nitrosylsulfuric acid with mechanical stirring. Throughout the addition, and for 30 minutes thereafter, the temperature is kept below 20°. Seven hundred milliliters of dry ether is added slowly with stirring, and the temperature of the mixture is kept at 0° for 1 hour. At the end of this period, the precipitation (aided by scratching) of the crystalline 4-nitronaphthalene-1-diazonium sulfate is complete (Note 1). This precipitate is collected, washed with ether and then with 95% ethanol until all the acid is removed, and finally dissolved in 100 ml. of iced water.

A saturated aqueous solution containing 50 g. of crystalline copper sulfate is treated with a similar solution of 50 g. of crystallized sodium sulfite. The greenish brown precipitate is collected, washed with water (Note 2), and then stirred into a solution of 100 g. (1.45 moles) of sodium nitrite in 400 ml. of water contained in a 2-l. beaker provided with an efficient mechanical stirrer.

The cold aqueous solution of the diazonium salt is then added slowly to the decomposition mixture. Considerable frothing occurs, and 4–5 ml. of ether is added from time to time to break the foam. After stirring for 1 hour (Note 3), the mixture is filtered and the crude dark brown precipitate of the 1,4-dinitronaphthalene is washed several times with water, then with 2% aqueous sodium hydroxide, and again with water. The precipitate is dried and extracted three times with boiling 95% ethanol (450 ml. in all). The extract is concentrated to 75 ml.; most of the 1,4-dinitronaphthalene separates and is collected. Additional amounts can be obtained by further concentration. The resulting product melts at 130–132° and weighs 6.0–7.0 g. (52–60%). The product can be purified either by steam distillation (Note 4) or by recrystallization from aqueous ethanol. Pale yellow needles melting at 134° are obtained (Note 5) and (Note 6).

## 2. Notes

1. This precipitate is sometimes sticky. It can be made granular by treating it with a small amount of 95% ethanol (after the removal of the supernatant liquid). Alternatively, it may suffice to keep the ethereal diazotized solution cold and scratch the sides of the beaker with a glass rod.

2. The cupro-cupri sulfite of this variety is more efficient as a decomposition reagent than the red-violet precipitate obtained by treating a hot solution of copper sulfate with a solution of ammonium sulfite saturated with sulfur dioxide and subsequently heating the mixture for 10 minutes at 90°.

3. The decomposition appears to be immediate, and at the end of 1 hour most of the inorganic material has passed into solution.

4. Steam distillation of 1,4-dinitronaphthalene is very slow. However, the cupro-cupri sulfite method[1] is a general one for the replacement of the diazonium group by the nitro group, and steam distillation is preferable whenever the product is readily volatile.

5. The solution is decolorized with charcoal in the course of the recrystallization. The checkers obtained 5 g. (43%) of golden needles after three recrystallizations.

6. 1,2-Dinitronaphthalene may be obtained similarly from 2-nitro-1-naphthylamine, or less satisfactorily from 1-nitro-2-naphthylamine; 1,6- and 2,6-dinitronaphthalenes can be prepared from the 5-nitro- and 6-nitro-2-naphthylamines, respectively, by a modification of the process. Since the solubility of these amines in glacial acetic acid is slight, it is preferable to prepare the diazonium sulfate as follows: Ten grams of the amine is dissolved in 50 ml. of sulfuric acid (sp. gr. 1.84), and the solution is mixed with one of 10 g. of sodium nitrite in 50 ml. of sulfuric acid (sp. gr. 1.84). This mixture is stirred into 200 ml. of glacial acetic acid. The temperature is maintained below 20° throughout these operations. After 30 minutes, the diazonium sulfate is precipitated at 0° by the addition of 200–500 ml. of ether as previously described.

## 3. Discussion

1,4-Dinitronaphthalene has been prepared previously from diazotized 4-nitro-1-naphthylamine by a modified Sandmeyer procedure,[2,3] from 5,8-dinitrotetralin by dehydrogenation,[4] by the deamination of 1,4-dinitro-2-naphthylamine,[5] and by the decomposition of 4-nitro-1-naphthalenediazonium cobaltinitrite.[6] The method described above has been published.[1]

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## References and Notes

1. Hodgson, Mahadevan, and Ward, *J. Chem. Soc.*, **1947**, 1392.
2. Vesely and Dvorak, *Bull. soc. chim. France*, **33**, 319 (1923).
3. Contardi and Mor, *Rend. ist. lombardo sci.*, **57**, 646 (1924) [*C. A.*, **19**, 827 (1925)].
4. Chudozilov, *Collection Czechoslov. Chem. Commun.*, **1**, 302 (1929) [*C. A.*, **23**, 4212 (1929)].
5. Hodgson and Hathway, *J. Chem. Soc.*, **1945**, 453.
6. Hodgson and Ward, *J. Chem. Soc.*, **1947**, 127.

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

diazonium sulfate

cupro-cupri sulfite

1,6- and 2,6-dinitronaphthalenes

5-nitro- and 6-nitro-2-naphthylamines

4-nitro-1-naphthalenediazonium cobaltinitrite

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ether (60-29-7)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

copper sulfate (7758-98-7)

sodium nitrite (7632-00-0)

charcoal (7782-42-5)

nitrosylsulfuric acid (7782-78-7)

1,4-Dinitronaphthalene,
Naphthalene, 1,4-dinitro- (6921-26-2)

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

4-nitronaphthalene-1-diazonium sulfate

ammonium sulfite (10196-04-0)

1,2-Dinitronaphthalene

2-nitro-1-naphthylamine (607-23-8)

1-nitro-2-naphthylamine

5,8-dinitrotetralin

1,4-dinitro-2-naphthylamine