



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.

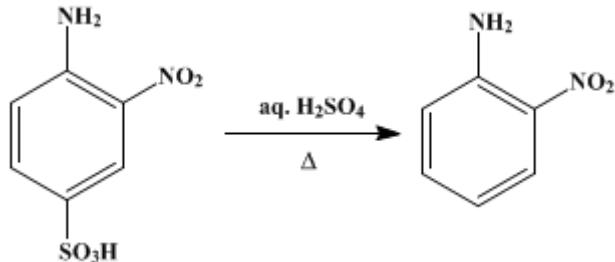
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.388 (1941); Vol. 9, p.64 (1929).

***o*-NITROANILINE**

[Aniline, *o*-nitro-]



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Checked by Roger Adams and S. V. Puntambeker.

1. Procedure

In a 3-l. round-bottomed flask fitted with a reflux condenser are placed 218 g. (1 mole) of coarsely powdered technical *o*-nitroaniline-*p*-sulfonic acid, and a hot mixture of 775 cc. of concentrated sulfuric acid (sp. gr. 1.84) and 950 cc. of water (Note 1). Heat is applied and the mixture is refluxed gently for one hour after solution is practically complete (total about three hours). The resulting dark solution is allowed to cool and is poured slowly into 12 l. of cold water in a crock (Note 2).

After cooling, the dense orange-yellow precipitate is filtered with suction. This crop of crystals after air-drying weighs about 70 g. and melts at 68–70°. The filtrate is returned to the crock and made slightly alkaline with 50 per cent sodium hydroxide solution (about 2.25 l.). It is then made barely acid to litmus with sulfuric acid. This neutralization will produce considerable heat, and the mixture should be thoroughly cooled before filtering. This second crop of crystals weighs about 22–25 g. and melts at 69–70.5°. The total crude yield is 90–95 g.

The two crops of crystals may be combined for recrystallization from boiling water, using 1 l. for each 9 g. The hot solution is filtered quickly, and the filtrate is cooled thoroughly and filtered with suction. The crystals are dried at 50°. The product melts at 69–71°. An alternative method of purification is to dissolve the crude product in about 250 cc. of 95 per cent alcohol, filter the solution, dilute with 1 l. of hot water, and warm on a steam bath if a precipitate forms. On cooling this solution, the product separates in orange-brown needles, and is filtered and air-dried. The yield is about 78 g. (56 per cent of the theoretical amount), m.p. 69.5–70.5°.

2. Notes

1. If cold, diluted acid is used, stirring must be employed during the heating to prevent caking and consequent charring.
2. The dark solution may be poured slowly over sufficient ice to half-fill a 16-l. (4-gallon) crock. A good yield was obtained in this way, but at this point the temperature is not likely to rise much and the use of cold water is less expensive and sufficiently satisfactory.

3. Discussion

o-Nitroaniline can be obtained together with some *p*-nitroaniline in the nitration and subsequent hydrolysis of acetanilide¹ and of benzanilide²; by the sulfonation, nitration, and subsequent hydrolysis of oxanilide³ and of acetanilide⁴; by the nitration of aniline and separation of the mixture of isomers;⁵ and by heating *o*-chloronitrobenzene with ammonium acetate.⁶

This preparation is referenced from:

References and Notes

1. Walker and Zincke, Ber. **5**, 114 (1872); Remsen and Graham, Am. Chem. J. **11**, 320 (1889); Weida, Am. Chem. J. **19**, 547 (1897); Pokorny, Bull. Soc. Indus. Mulhouse 280 (1894) [Chem. Zentr. II, 556 (1894)].
 2. Lellmann, Ann. **221**, 6 (1883).
 3. Anilinoel-Fabrik A. Wülfing, Ger. pat. 65,212; 66,060 [Frdl. **3**, 44, 45 (1892)].
 4. Nietzki and Benckiser, Ber. **18**, 295 (1885); Turner, Ber. **25**, 986 (1892); Sakellarios, Ber. **58**, 2286 (1925).
 5. Bruns, Ber. **28**, 1954 (1895).
 6. Soc. Chimique De La Grande-Paroisse, Brit. pat. 169,688 [C. A. **16**, 721 (1922)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

oxanilide

alcohol (64-17-5)

sulfuric acid (7664-93-9)

ammonium acetate (631-61-8)

aniline (62-53-3)

Acetanilide (103-84-4)

sodium hydroxide (1310-73-2)

Benzanilide (93-98-1)

o-chloronitrobenzene (88-73-3)

o-NITROANILINE,
Aniline, o-nitro- (88-74-4)

o-nitroaniline-p-sulfonic acid (616-84-2)

p-nitroaniline (100-01-6)