



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.

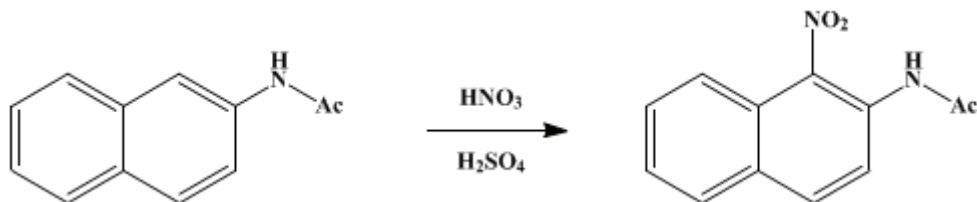
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.438 (1943); Vol. 13, p.72 (1933).

1-NITRO-2-ACETYLAMINONAPHTHALENE

[Acetamide, N-(1-nitro-2-naphthyl)-]



Submitted by W. W. Hartman and Lloyd A. Smith.

Checked by Louis F. Fieser and J. T. Walker.

1. Procedure

In a 2-l. round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel, and clamped in a position such that it may be surrounded by a bath of water and ice when desired, are placed 300 g. (1.62 moles) of β -acetylamino-naphthalene (m.p. 131–132°) and 500 cc. of glacial acetic acid. With the mixture at room temperature, the stirrer is set in motion, and 200 g. (143 cc., 2.1 moles) of concentrated nitric acid (sp. gr. 1.4) is added dropwise over a period of forty-five minutes; the temperature is kept below 40° by occasionally immersing the flask in the cooling bath. When about one-tenth of the nitric acid has been added, the reaction mixture sets to a mass that is stirred with difficulty. The addition of nitric acid is stopped at this point. After three to five minutes the mass becomes fluid, and the addition of nitric acid is resumed. When about one-fourth of the nitric acid has been added, all the solid material dissolves. Considerable heat is evolved at this point, and good cooling is required to keep the temperature from rising above 40°; the mixture must be cooled during the addition of the remainder of the acid. After the addition is complete, stirring is continued for ten minutes longer.

The flask is stoppered and cooled in a bath of ice and water for three hours; the reaction product should then separate in the form of a yellow, crystalline paste (Note 1) and (Note 2). The crystals are collected on a 19-cm. Büchner funnel and washed, first with 200 cc. of 50 per cent acetic acid, and next with 400 cc. of ordinary ether. This crude, dry product, weighing 270–290 g., is placed in a 3-l. flask and heated under a reflux condenser with 1.7 l. of benzene for twenty minutes. The mixture is then allowed to cool to 40–45° and filtered through a 19-cm. Büchner funnel. The residue is a mixture of sparingly soluble isomers, chiefly 5- and 8-nitro-2-acetylamino-naphthalene. On further cooling of the filtered solution, there is obtained 190–200 g. of 1-nitro-2-acetylamino-naphthalene melting at 117–119°. This material is recrystallized from about 500 cc. of hot 95 per cent ethyl alcohol. Fine yellow crystals melting at 123–124° are obtained. The yield is 175–182 g. (47–49 per cent of the theoretical amount).

2. Notes

1. The material is sometimes slow in crystallizing, and it is then advisable to scratch the walls of the container with a stirring rod. If this fails to induce crystallization, seed may be obtained by diluting a small portion of the solution with water.
2. Crystallization is nearly, but not entirely, complete after this period of time. When the mother liquor was allowed to stand for five days, an additional quantity of material separated. From this material only 3 g. of pure 1-nitro-2-acetylamino-naphthalene was obtained.

3. Discussion

This procedure is based upon previous studies of the nitration of 2-acetylamino-naphthalene.¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 451](#)

References and Notes

1. Jacobson, *Ber.* **14**, 803 (1881); Liebermann and Jacobson, *Ann.* **211**, 44 (1882); Friedlaender and Littner, *Ber.* **48**, 328 (1915); Schiemann and Ley, *ibid.* **69**, 963 (1936).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

5- and 8-nitro-2-acetylaminonaphthalene

[ethyl alcohol \(64-17-5\)](#)

[acetic acid \(64-19-7\)](#)

[Benzene \(71-43-2\)](#)

[ether \(60-29-7\)](#)

[nitric acid \(7697-37-2\)](#)

[1-Nitro-2-acetylaminonaphthalene,
Acetamide, N-\(1-nitro-2-naphthyl\)- \(5419-82-9\)](#)

[β-acetylaminonaphthalene,
2-acetylaminonaphthalene \(581-97-5\)](#)