



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.

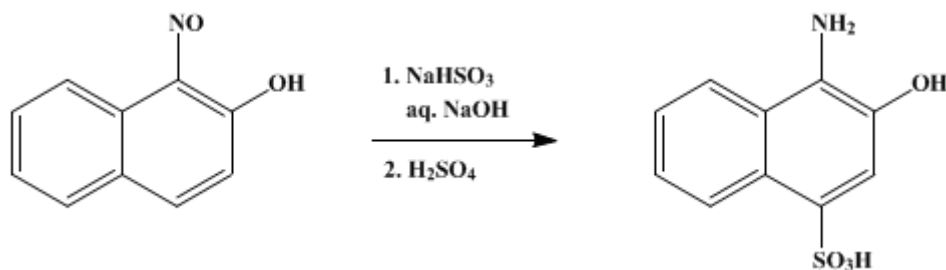
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.42 (1943); Vol. 11, p.12 (1931).

1-AMINO-2-NAPHTHOL-4-SULFONIC ACID

[2-Naphthol-4-sulfonic acid, 1-amino-]



Submitted by Louis F. Fieser

Checked by Frank C. Whitmore and D. J. Loder.

1. Procedure

Three hundred grams of β -naphthol (2.1 moles) is converted into nitroso- β -naphthol (*Org. Syn. Coll. Vol. I, 1941, 411*) (*Note 1*), and the product is transferred to a 6-l. (1.5 gal.) crock which is wide enough to admit the Büchner funnel (30-cm.) employed. A cold solution of 600 g. (5.8 moles) of sodium bisulfite and 100 cc. of 6 *N* sodium hydroxide solution in 2 l. of water (*Note 2*) is used to rinse the material adhering to the funnel into the crock. The mixture is diluted with water to 4–4.5 l. and stirred until solution of the nitroso- β -naphthol is complete (about fifteen minutes). The dark solution is siphoned onto a large Büchner funnel and filtered by suction, thus removing a small amount of tarry material which is always present. The clear, yellowish brown filtrate is transferred to an 8- to 10-l. wide-mouthed bottle and diluted with water to 7 l. While the solution is vigorously stirred, 400 cc. of concentrated sulfuric acid is poured slowly down the walls of the bottle; the mixture is then placed in the hood and protected from the light (*Note 3*). The temperature rises from 20–25° to 35–40° at once and to about 50° in the course of two hours, when the reaction is nearly complete. After standing for a total of five hours or more (*Note 4*), the precipitate, which sets to a stiff paste in the bottle, is collected on a filter. The residue is transferred to a 1-l. beaker and washed with 200 cc. of water. The mixture is filtered, and the residue is washed with 300 cc. of water on the filter. The moist material weighs 700–800 g. No appreciable decomposition takes place on drying the product to constant weight at 120°. A light powder of fine, gray needles is thus obtained. The yield is 410–420 g. (82–84 per cent of the theoretical amount based on the β -naphthol used) (*Note 5*).

2. Notes

1. In preparing nitroso- β -naphthol in the quantity here required it is convenient to use a 7- to 8-l. bottle, with an 8- to 10-cm. opening, equipped with a stirrer of heavy glass rod having four or five right-angle bends which extend to the top of the bottle and which are just small enough to fit the mouth. The bottle is placed in a bucket containing a salt-ice mixture which is stirred occasionally by hand. With this arrangement a temperature of 0° may be maintained without internal cooling.

2. Sodium hydroxide is added to the bisulfite solution in order to neutralize any acid which has not been removed by washing, and which would liberate sulfur dioxide and thus cause some reduction of the nitroso compound before the addition product is formed. An excess of alkali, as employed above, aids in the solution of the material.

3. The aminonaphtholsulfonic acid becomes rose colored on long exposure to the light, especially when moist.

4. The time required for the process may be shortened somewhat by adding the sodium bisulfite-sodium hydroxide solution to the suspension of the crude nitroso compound, thus avoiding a long filtration. The amounts of water employed in the various operations should be reduced to a minimum, and enough additional sodium hydroxide solution should be used to neutralize the excess acid present. The product

is of a slightly inferior quality, and the yield is 4–5 per cent lower.

5. This gray material is not quite pure and contains water of crystallization so that the percentage yield reported is in error. A better product can be obtained by stirring the mixture of [nitroso-β-naphthol](#) and [sodium bisulfite](#) solution vigorously by hand with a wooden paddle thus causing all the soluble product to dissolve in three to four minutes. The suspension is then filtered as rapidly as possible using two 15-cm. Büchner funnels and changing filter papers frequently. The clear, golden-yellow filtrate is acidified immediately on completion of the filtration. The product is then light gray, whereas, if much time elapses before the bisulfite solution is acidified, the solution turns red and the [aminonaphtholsulfonic acid](#) may be deep purple-gray in color. After the product has been collected and washed with water, it is washed with warm [alcohol](#) until the filtrate is colorless, 1.5–2 l. being required. The product is washed with two 100-cc. portions of [ether](#) and dried to constant weight at 60–80° in the absence of light. A pure white, dust-dry product is thus obtained, weighing 370–380 g. (75–78 per cent of the theoretical amount based on the [β-naphthol](#)). The wash alcohol does not dissolve an appreciable amount of the [aminonaphtholsulfonic acid](#) since evaporation of the deep red wash liquor gives a dark residue weighing only 3–4 g. (E. L. Martin and Louis F. Fieser, private communication.)

3. Discussion

1-Amino-2-naphthol-4-sulfonic acid has been prepared by warming 2-naphthoquinone-1-chloroimide with [sodium bisulfite](#) solution;¹ by reduction of 1-benzeneazo-2-naphthol-4-sulfonic acid with [stannous chloride](#) and [hydrochloric acid](#);² by treatment of 1-amino-2-naphthol hydrochloride with [sodium sulfite](#);³ and by treatment of [nitroso-β-naphthol](#) with [sodium bisulfite](#) and [hydrochloric acid](#).⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 633](#)

References and Notes

1. Friedländer and Reinhardt, *Ber.* **27**, 241 (1894).
2. Marschalk, *Bull. soc. chim.* (4) **45**, 660 (1929).
3. Marschalk, *ibid.* (4) **45**, 662 (1929).
4. Schmidt, *J. prakt. Chem.* (2) **44**, 522 (1891); Böniger, *Ber.* **27**, 23 (1894).

Appendix

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

2-naphthoquinone-1-chloroimide

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

[sulfuric acid](#) (7664-93-9)

[hydrochloric acid](#) (7647-01-0)

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

[sodium sulfite](#) (7757-83-7)

[sodium hydroxide](#) (1310-73-2)

sulfur dioxide (7446-09-5)

β -naphthol (135-19-3)

stannous chloride

sodium bisulfite (7631-90-5)

Nitroso- β -naphthol (131-91-9)

1-amino-2-naphthol hydrochloride (1198-27-2)

1-AMINO-2-NAPHTHOL-4-SULFONIC ACID,
2-Naphthol-4-sulfonic acid, 1-amino- (116-63-2)

aminonaphtholsulfonic acid

sodium bisulfite-sodium hydroxide

1-benzeneazo-2-naphthol-4-sulfonic acid