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.

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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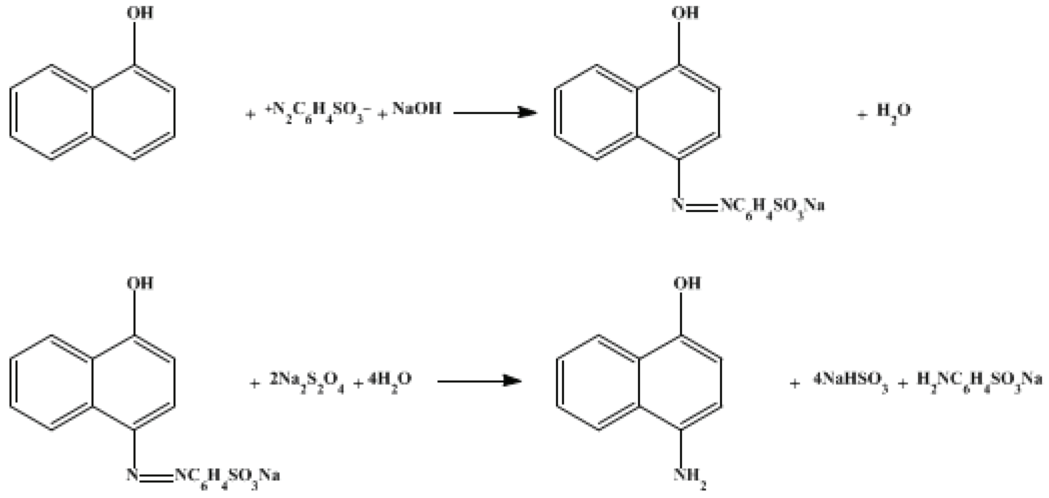
1,4-AMINONAPHTHOL HYDROCHLORIDE

[1-Naphthol, 4-amino-, hydrochloride]



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1. Procedure

One hundred and five grams (0.5 mole) of sulfanilic acid dihydrate is diazotized exactly as described in the last paragraph of p. 35. While the suspension of *p*-benzenediazonium sulfonate is kept in an ice bath, 72 g. (0.5 mole) of α-naphthol (Note 1) is dissolved in the warm solution obtained by dissolving 110 g. (2.75 moles) of sodium hydroxide in 600 cc. of water in a 5-l. flask. The naphthoxide solution is cooled to 25°, 400 g. of ice is added, and the suspension of the diazonium salt is then introduced (Note 2). The mixture is stirred well and allowed to stand for one hour, during which time the formation of the dye, Orange I, goes to completion.

The deep purple-red solution of Orange I is warmed to 45–50°, about one-tenth of 230 g. (about 1.1 moles) of technical sodium hydrosulfite (Note 3) is added cautiously, and the mixture is stirred until the froth subsides; the remainder of the hydrosulfite is then added without delay. The tan suspension of the aminonaphthol is heated to about 70° to effect sufficient coagulation to permit filtering. It is then cooled quickly to 25° by stirring in an ice bath, and the precipitate is filtered and washed with fresh 1 per cent sodium hydrosulfite solution.

The crude aminonaphthol is transferred quickly to a beaker containing a solution of 2 g. of stannous chloride dihydrate and 63 cc. of hydrochloric acid in 800 cc. of water at 30°. On stirring and warming, the amine dissolves. The solution, which is usually a deep red, is filtered with suction; treatment with charcoal is not necessary. One hundred cubic centimeters of concentrated hydrochloric acid is added, the solution is heated to boiling for five to ten minutes, and a second 100-cc. portion of the acid is added. During this heating the color fades to a light yellow, and on cooling to 0° a mass of small, nearly colorless crystals is obtained.

This material (dry weight, 77–80 g.) (Note 4), without being dried, is dissolved by heating in a solution of 2 g. of stannous chloride and 2 cc. of concentrated hydrochloric acid in 700 cc. of water. The hot solution is clarified by filtration through a 5-mm. mat of decolorizing carbon. One hundred cubic centimeters of concentrated hydrochloric acid is added to the hot solution, which is then cooled in an ice bath, treated with a second 100-cc. portion of acid, and cooled to 0°. The precipitate is filtered and washed with a cold solution of 50 cc. of concentrated hydrochloric acid in 200 cc. of water. The 1,4-aminonaphthol hydrochloride forms small, nearly colorless needles of a high degree of purity. The solution in water is faintly pink, and the crystals may acquire a slight pink color after a few weeks. The yield is 70–73 g. (72–75 per cent of the theoretical amount) (Note 5).

2. Notes

1. The α-naphthol should be free from the β-isomer; if the material is very highly colored it is advisable to purify it by distillation at atmospheric pressure. Material melting at 95–96° is satisfactory.
2. A low temperature is required during the coupling in order to avoid the formation of the disazo compound.
3. If the hydrosulfite is of poor quality more will be needed, and an additional amount of sodium hydroxide should also be added.
4. The material is slightly yellow and may redden on drying; it probably contains a trace of 2,4-diamino-1-naphthol.
5. These directions are very similar to the directions on p. 35 for preparing 1,2-aminonaphthol and should be compared with those directions. The differences between the two procedures are the result of the greater solubility and the greater sensitivity to air oxidation of the 1,4-aminonaphthol.

3. Discussion

The usual method of preparing 1,4-aminonaphthol has been from α-naphthol through an azo dye. The majority of investigators have reduced technical Orange I with stannous chloride;[1], [2], [3], [4], [5], [6] benzeneazo-α-naphthol has been reduced by the same reagent.[7], [8] In order to make possible the use of crude technical α-naphthol a method has been developed[9] for the preparation of the benzeneazo compound, its separation from the isomeric dye coming from the β-naphthol present as well as from any disazo compound by extraction with alkali, and the reduction of the azo compound in alkaline solution with sodium hydrosulfite. The process, however, is tedious and yields an impure product.

1,4-Aminonaphthol can be prepared by reduction of 1,4-nitrosonaphthol, but this is not practical because the starting material is not readily available.[7] The aminonaphthol can also be prepared with a 60 per cent overall yield by the reduction of α-nitronaphthalene to the naphthyl hydroxylamine and rearrangement of the hydroxylamine.[10]

The method described above is applicable with slight modifications to the preparation of both the ortho and para aminonaphthols and to many homologs, benzologs, and heterocyclic isologs of these substances. The chief feature of novelty is in the use of stannous chloride as an anti-oxidant in preparing and crystallizing the amine hydrochlorides.[11]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

1,4-Aminonaphthol hydrochloride

1,4-Aminonaphthol

1,4-nitrosonaphthol

1,2-aminonaphthol

Orange I

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

1-Naphthol, 4-amino-, hydrochloride (5959-56-8)

α-naphthol (90-15-3)

benzeneazo-α-naphthol

sodium hydrosulfite (7775-14-6)

aminonaphthol

β-naphthol (135-19-3)

stannous chloride

α-nitronaphthalene (86-57-7)

sulfanilic acid dihydrate

stannous chloride dihydrate (10025-69-1)

2,4-diamino-1-naphthol

naphthyl hydroxylamine

p-benzenediazonium sulfonate (305-80-6)