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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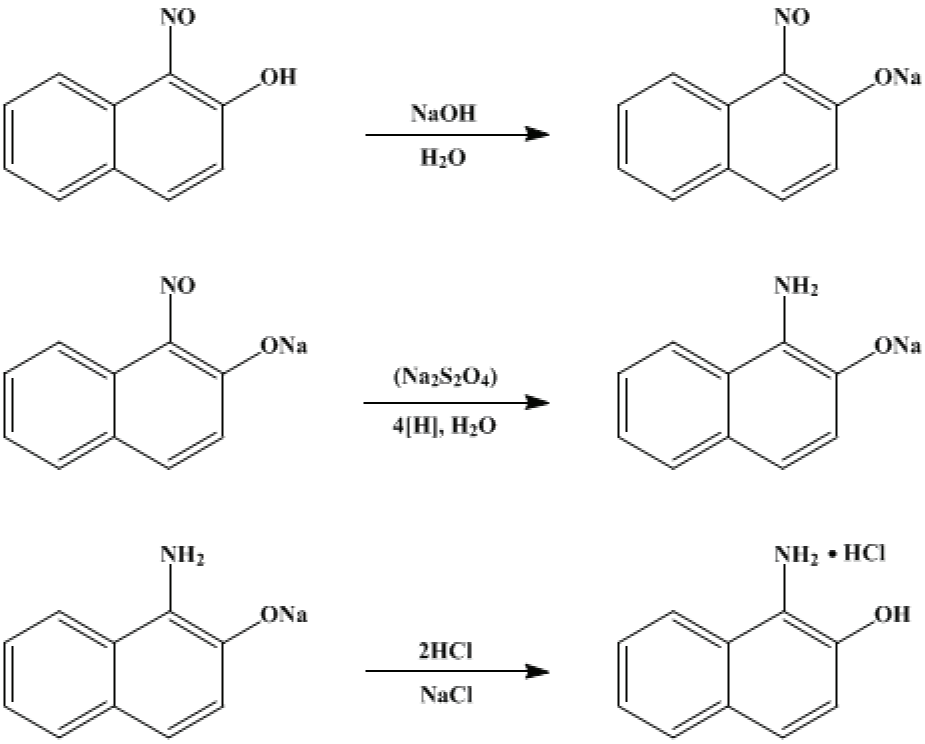
Organic Syntheses, Coll. Vol. 2, p.33 (1943); Vol. 17, p.9 (1937).

1,2-AMINONAPHTHOL HYDROCHLORIDE

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



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1. Procedure

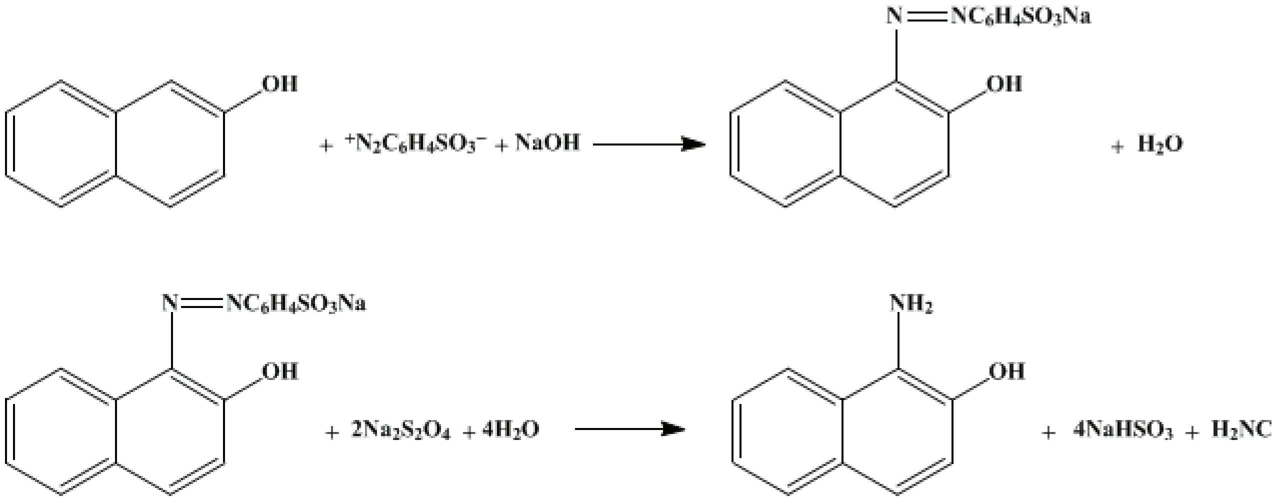
In an 8-l. (2-gal.) earthenware crock, equipped with a mechanical stirrer and a tube for introducing steam, are placed 240 g. (1.39 moles) of nitroso-β-naphthol (from 200 g. of β-naphthol, Org. Syn. Coll. Vol. I, **1941**, 411) (Note 1), 1.5 l. of water, and 300 cc. of 5 *N* sodium hydroxide. The lumps are broken up with a rod, and the mixture is stirred for about thirty minutes. At the end of this time, practically all the nitroso compound is dissolved and 1.2 l. of 5 *N* sodium hydroxide is added. Steam is passed in until the temperature of the mixture is 35°, and then the steam is shut off and 600 g. of technical sodium hydrosulfite (at least 85 per cent pure) is added while the solution is being stirred. The solution is stirred continuously for five minutes while the temperature rises to 60–65°, and then for one minute at five-minute intervals during one-half hour. At the end of about fifteen minutes the solution becomes clear and light yellow in color. A small amount of black scum floats on the surface.

The solution is now cooled to 20° by the addition of about 1 kg. of ice and 500 cc. of technical concentrated hydrochloric acid (sp. gr. 1.16) is added with stirring. This precipitates the aminonaphthol as a voluminous, almost white precipitate (Note 2) which is collected on two 20-cm. Büchner funnels. It is rapidly pressed as free from mother liquor as possible and transferred quickly (Note 3) to an 8-l. (2-gal.) crock containing 2.5 l. of water and 250 cc. of technical concentrated hydrochloric acid. The large lumps are broken up with a rod, steam is passed in, and the stirrer is started. Steam is introduced at such a rate that a temperature of 85–90° is reached within ten minutes; the mixture is stirred at this temperature for one hour longer. The hot mixture is then filtered through a 15-cm. Büchner funnel, and the filtrate is cooled to 35–40° in an ice bath.

The claret-colored solution (5.2–5.8 l.) is filtered through a fluted filter paper in a 15-cm. funnel into 1.2 l. of concentrated hydrochloric acid in an 8-l. bottle. The aminonaphthol hydrochloride starts to precipitate immediately. The mixture is allowed to stand for at least two hours with occasional agitation to ensure complete precipitation. The hydrochloride is collected on a 15-cm. Büchner funnel and washed successively with three small portions of 20 per cent hydrochloric acid and three 50-cc. portions of ether (Note 4). It is then dried in the air in thin layers on filter paper. The yield is 180–200 g. of anhydrous material (Note 5) (66–74 per cent of the theoretical amount based on 200 g. of β-naphthol). The hydrochloride is unstable; in solution it decomposes rapidly, but this decomposition can largely be prevented by the addition of sodium bisulfite. The dry solid slowly changes and should be used within a few weeks of its preparation (Note 6).

2. Notes

1. It is usually not convenient to dry the nitroso-β-naphthol. The amount given in these directions corresponds to 200 g. of β-naphthol, and the yield is calculated on this basis. The nitroso-β-naphthol dissolves in one mole of sodium hydroxide, forming a green solution. There is left in suspension a small amount of amorphous brown material which need not be removed.
2. The amounts of sodium hydroxide, sodium hydrosulfite, and hydrochloric acid used are such that complete precipitation of the aminonaphthol results at this point. It is well to test for complete precipitation, however, by adding a few drops of alkali to one portion of the filtrate and a little acid to another.
3. The aminonaphthol is very sensitive to atmospheric oxidation. When first precipitated it is white, but it becomes purple in the air and therefore should be handled rapidly. A small amount of sodium bisulfite may be added at this point to decrease the oxidation, but this is usually unnecessary since some bisulfite from the reduction adheres to the precipitate and is carried through to the final precipitation.
4. Washing with ether greatly facilitates the drying of the product and also lightens its color somewhat. If the material is to be used without being dried, the washing with ether may be omitted.
5. Air-dried material, when apparently completely dry, contains 10–15 per cent of moisture. In order to obtain the true weight of the material an aliquot sample should be dried over sodium hydroxide under reduced pressure.
6. The product, as first formed, is a very light purple but darkens on long standing. It may be purified by dissolving in hot water containing sodium bisulfite, filtering, and reprecipitating with hydrochloric acid.



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1. Procedure

(*A*) *Diazotization of Sulfanilic Acid*.—A mixture of 105 g. (0.5 mole) of sulfanilic acid dihydrate, 26.5 g. (0.25 mole) of anhydrous sodium carbonate, and 500 cc. of water is heated and stirred until all the sulfanilic acid has dissolved, and the solution is then cooled in an ice bath to 15° (sodium sulfanilate begins to crystallize at this temperature). A solution of 37 g. (0.54 mole) of sodium nitrite in 100 cc. of water is added and the resulting solution is poured at once onto a mixture of 106 cc. (1.25 moles) (Note 1) of concentrated hydrochloric acid (sp. gr. 1.18) and 600 g. of ice contained in a 2-l. beaker. The solution, from which *p*-benzenediazonium sulfonate separates on stirring, is allowed to stand in an ice bath for fifteen to twenty-five minutes, during which time the naphthoxide solution is prepared.

(*B*) *Coupling: Orange II.*—Seventy-two grams of β-naphthol (0.5 mole) is dissolved in the warm solution obtained by dissolving 110 g. (2.75 moles) (Note 2) of sodium hydroxide in 600 cc. of water in a 5-l. flask, and the solution is cooled to about 5° by the addition of 400 g. of ice. The suspension of the diazonium salt then is added and the mixture is stirred well and allowed to stand without external cooling for one hour (Note 3). The azo compound soon separates from the red solution and eventually forms a stiff paste.

(*C*) *Reduction: 1,2-Aminonaphthol Hydrochloride.*—The suspension of Orange II is heated to 45–50°, when all the material dissolves with slight evolution of gas. About one-tenth of 230 g. (about 1.1 moles) of technical sodium hydrosulfite (Note 4) is added cautiously and the mixture is stirred until the froth subsides; the remainder is then added without delay. The yellow material which first separates (probably the hydrazo compound) soon is converted into the nearly colorless aminonaphthol. In order to complete the reduction and to give an easily filterable product the mixture is heated strongly until it begins to froth; it is then cooled to 25° by stirring in an ice bath, and the pink or cream-colored product is collected and washed free from the slightly yellow mother liquor with water.

The crude aminonaphthol is washed into a beaker containing a solution at 30° of 2 g. of stannous chloride dihydrate and 53 cc. (0.63 mole) of concentrated hydrochloric acid in 1 l. of water. When the mixture is stirred the amine soon dissolves, leaving in suspension a small amount of fluffy material which is easily distinguishable from the original lumps (Note 5). The solution is clarified by stirring (without heating) for five minutes with 10 g. of decolorizing carbon, and it is then filtered by suction. The pale yellow solution is treated with 50 cc. of concentrated hydrochloric acid and heated to the boiling point, a second 50 cc. of the acid being added as the heating progresses. The color becomes somewhat fainter during this process. The vessel containing the hot solution is transferred to an ice bath and allowed to cool undisturbed, and the 1-amino-2-naphthol hydrochloride soon separates in the form of large, perfectly colorless needles. When fairly cold, 100 cc. of concentrated hydrochloric acid is added and the solution is cooled to 0° before collecting the product (Note 6). The hydrochloride is washed with a cold solution of 50 cc. of concentrated hydrochloric acid in 200 cc. of water and dried on a filter paper at a temperature not above 30–35°. The yield is 70–83 g. (72–85 per cent of the theoretical amount). The material will remain colorless, or very nearly so, if protected from the light in storage. The fresh solution in water is only faintly colored and leaves but a trace of residue on filtration.

Although this material is suitable for most purposes, it may be purified further in the following manner. It is dissolved by heating in a solution of 2 g. of stannous chloride and 2 cc. of concentrated hydrochloric acid in 1 l. of water, and the hot solution is clarified by filtration through a 5-mm. mat of decolorizing carbon (Note 7). The yellow or red color which may develop disappears on reheating to the boiling point. After the addition of 100 cc. of concentrated hydrochloric acid the solution is allowed to cool in an ice bath, treated with a second 100 cc. of acid, cooled to 0°, and collected and washed as before. The crystalline product is colorless, ash-free, and of analytical purity. The loss in the crystallization of an 80-g. lot amounts to 5–10 g. (6–12 per cent).

2. Notes

1. Diazotization can be accomplished by the use of just one equivalent of acid (0.5 mole), but the solution of the diazoic acid, $NaO_3SC_6H_4N{=}NOH$, so formed is much less stable than the suspension of the inner salt which results from the use of more acid.
2. The excess alkali is not required for the process of coupling, but rather to provide conditions suitable for the reduction.
3. The yield is not improved by allowing a longer period for the reaction. Under the conditions specified, the mixture during the coupling remains at a temperature of 5–10°.
4. If the hydrosulfite is of poor quality more will be needed, and an additional amount of sodium hydroxide should also be added.

5. The solution is highly supersaturated, but it will remain so unless allowed to stand for an undue amount of time. It is also a mistake to add the quantity of concentrated hydrochloric acid specified to a suspension of the aminonaphthol, for this may initiate crystallization.
6. An alternative method of crystallization is to add all the hydrochloric acid (200 cc.) to the boiling solution and to allow this to cool slowly; very large, thick needles result. In the presence of stannous chloride there is no danger of a darkening of the solution as the result of oxidation.
7. This method is preferable to the usual one when dealing with a substance sensitive to air oxidation.

3. Discussion

1-Amino-2-naphthol has been obtained from β-naphthylamine[1] and, more practically, from β-naphthol through the nitroso compound or an azo compound. Nitroso-β-naphthol has been reduced in alkaline solution with hydrogen sulfide[2], [3] or sodium hydrosulfite,[4] but early workers encountered difficulty in converting the amine into its hydrochloride without undue oxidation. Sulfur dioxide was employed as an anti-oxidant, but it is wholly inadequate. Reduction in an acidic medium, usually with stannous chloride, has been more satisfactory. The isolalation of the amine stannochloride and its tedious decomposition with hydrogen sulfide[5] are unnecessary, for the amine hydrochloride can be caused to crystallize essentially free from tin by avoiding an excess of the reducing agent.[2], [6], [7] Nitroso-β-naphthol has been reduced also with zinc dust and sulfuric acid,[8] but the quality of the material, used for conversion to the quinone, is in some doubt.

The nitroso derivative has disadvantages as an intermediate in that it involves handling either a voluminous precipitate or a large volume of solution, and in that some tar is likely to form; hence an azo compound is preferable. Technical Orange II has been reduced in a neutral or alkaline medium with sodium sulfide[2] or sodium hydrosulfite,[9] the sulfanilic acid being eliminated as the soluble sodium salt. With stannous chloride, the necessity of isolating the amine stannochloride[1] can be avoided by using just the calculated amount of reagent, the resulting mixture of amine hydrochloride and sulfanilic acid being separated with an alkaline buffer.[2] Witt[10] found that the sulfanilic acid can be kept in solution if this is sufficiently acidic, and with this improvement Russig[11] worked out a procedure for the preparation and reduction of Orange II which was reported to give excellent yields but which, judging from the results of conversion to the quinone, affords a poor product.

Orange II also has been reduced with zinc dust and hydrochloric acid,[12] by electrolysis,[13] and by catalytic hydrogenation,[14] while a number of other azo dyes derived from β-naphthol have been reduced to 1,2-aminonaphthol with hydrogen and Raney nickel.[15]

The method described above is novel chiefly in that it makes use of stannous chloride as an antioxidant in preparing and crystallizing the amine hydrochloride. The method is applicable with slight modifications to the preparation of many other aminophenols.[16]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 39
- Org. Syn. Coll. Vol. 2, 430

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Appendix

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

1,2-Aminonaphthol hydrochloride

Orange II

$NaO_3SC_6H_4N{=}NOH$

1,2-aminonaphthol

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

hydrogen sulfide (7783-06-4)

sodium carbonate (497-19-8)

sulfur dioxide (7446-09-5)

sodium nitrite (7632-00-0)

sodium hydrosulfite (7775-14-6)

aminonaphthol

aminonaphthol hydrochloride (41772-23-0)

β-naphthol (135-19-3)

stannous chloride

sodium bisulfite (7631-90-5)

Raney nickel (7440-02-0)

decolorizing carbon (7782-42-5)

zinc (7440-66-6)

sodium sulfide (1313-82-2)

Quinone (106-51-4)

Nitroso-β-naphthol (131-91-9)

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

sulfanilic acid dihydrate

stannous chloride dihydrate (10025-69-1)

sulfanilic acid (121-57-3)

β-naphthylamine (91-59-8)

sodium sulfanilate

1-Amino-2-naphthol

p-benzenediazonium sulfonate (305-80-6)