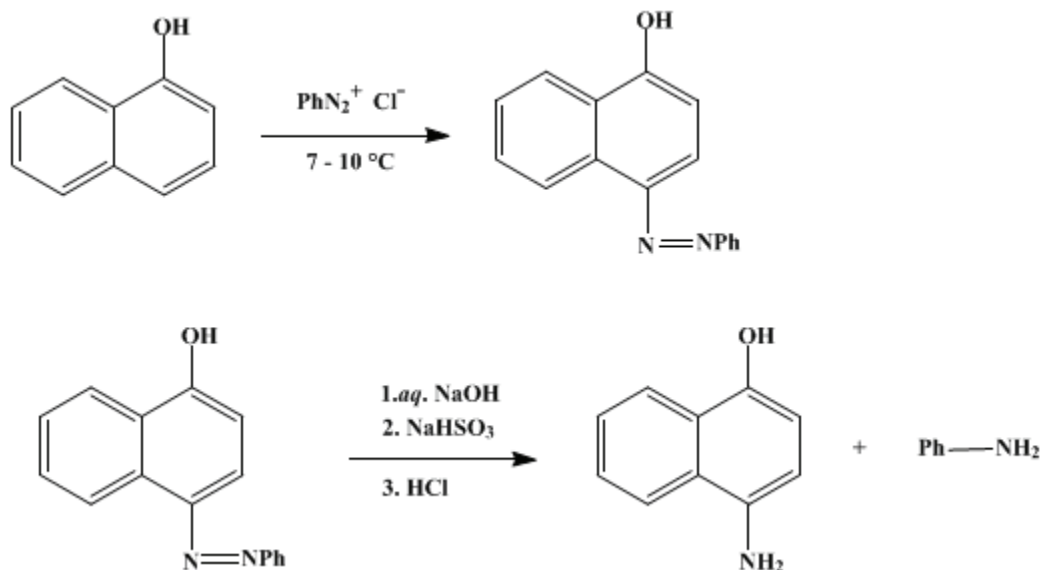


1,4-AMINONAPHTHOL HYDROCHLORIDE

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



Submitted by J. B. Conant, R. E. Lutz, and B. B. Corson.

Checked by H. T. Clarke and J. H. Bishop.

1. Procedure

In a 6-l. wide-mouthed bottle, fitted with a mechanical stirrer and a separatory funnel, are placed 200 g. (1.39 moles) of α -naphthol melting at 91° or higher (Note 1) and 910 cc. of 10 per cent sodium hydroxide solution (2.5 moles). The mixture is stirred for ten minutes, at the end of which time it has become a homogeneous solution.

While the naphthol is dissolving, a solution of benzenediazonium chloride is prepared. In a 3-l. wide-mouthed bottle are placed 128 g. (125 cc., 1.38 moles) of aniline and 1.5 kg. of cracked ice (Note 2), and upon this mixture while it is stirred (by hand) is poured 410 cc. of concentrated hydrochloric acid (31.5 per cent; sp. gr. 1.16). Some crystals of aniline hydrochloride separate at this point. A solution of 100 g. (1.45 moles) of sodium nitrite in 200 cc. of water is now run in slowly from a 500-cc. separatory funnel. The tip of the stem of the separatory funnel should dip well below the surface of the liquid. The mixture is stirred (by hand if desired) and a drop is tested from time to time with starch-iodide paper. This is best done by diluting the test-drop on a watch glass with about 1 cc. of water and then placing a drop of this solution on the starch-iodide paper. The sodium nitrite solution is added until there is a test for nitrous acid which is permanent for five minutes. The diazotization is then complete; all but 2-5 per cent of the nitrite is required.

To the alkaline solution of α -naphthol is now added 1 kg. of cracked ice, the stirrer is started and the diazonium solution run in through a separatory funnel, the stem of which dips below the surface of the solution. The stirring must be uniform and efficient during the addition (Note 3). The addition of the diazonium solution should take ten minutes. Ice is added if necessary to keep the solution below 10° . The mixture is stirred for one-half hour after the addition of the diazonium solution and then allowed to stand for three hours at $7-10^\circ$ (Note 4). It is then filtered on a Büchner funnel, washed with 1 l. of water and sucked as dry as possible.

The moist benzeneazo- α -naphthol is next transferred to a 5-l. wide-mouthed bottle or a 2-gallon (8-l.) crock equipped with a mechanical stirrer and containing 3 l. of 10 per cent sodium hydroxide solution. The mixture is stirred for ten minutes to insure solution of the dye, and then filtered. The

insoluble solid is stirred up with 500 cc. of 10 per cent [sodium hydroxide](#), filtered again and washed with water. The solid, which weighs 10–90 g., consists mainly of the 2,4-disazo derivative (m. p. 197–198°), together with any benzeazo- β -naphthol that may be present.

To the deep-red solution is added 550 g. of [sodium hydrosulfite](#) (of at least 80 per cent purity); the mixture is stirred for five minutes and then for five thirty-second periods during one-half hour ([Note 5](#)). The solution slowly loses its red color (a thin layer of [aniline](#) collects on the surface), and the temperature rises from 25–50°. At the end of one-half hour the solution should no longer be red; it is then rapidly cooled to 20° in a freezing bath and by the addition of about 500 g. of ice.

To the solution is now added, with stirring, 625 cc. (6.3 moles) of concentrated (31.5 per cent; sp. gr. 1.16) [hydrochloric acid](#) ([Note 6](#)) or its equivalent of acid of approximately the same strength. A cream-colored precipitate of the [aminonaphthol](#) forms. It is rapidly filtered off on a Büchner funnel ([Note 7](#)) and washed with one portion (200 cc.) of water about half saturated with [sulfur dioxide](#). The precipitate soon darkens on exposure to air and is therefore rapidly transferred to a 2-gallon (8-l.) crock containing 2 l. of water and 340 cc. of concentrated [hydrochloric acid](#). The soft lumps are broken up with a cork stopper set on the end of a stirring rod. Steam is passed into the mixture for forty-five minutes, and during the last thirty minutes the mixture is stirred mechanically. At the end of this time the amine will have passed completely into solution. An insoluble impurity weighing 25–30 g. is removed by filtering with suction. The filtrate is cooled to 25° and if it is not clear is filtered again. To the clear solution at 25° is added 1200 cc. of concentrated [hydrochloric acid](#) with stirring, when a light gray precipitate of the [aminonaphtholhydrochloride](#) immediately forms. The solution is allowed to stand for two to three hours and is then filtered with suction. The hydrochloride is sucked as free from mother liquor as possible, washed very thoroughly with [hydrochloric acid](#) (1 volume acid to 1 volume of water), and dried on a porous plate. The liquors are concentrated, under reduced pressure, to a small volume, and a second crop is thus obtained. The product is of a light purplish tint ([Note 8](#)) and weighs 175–200 g. (65–74 per cent of the theoretical amount, based on the quantity of α -naphthol employed) ([Note 9](#)).

2. Notes

1. Technical α -naphthol varies widely in purity, but material melting at 91° or above is substantially free of β -naphthol; unsatisfactory results will be obtained with material of an inferior grade, but when not more than 2 per cent of β -naphthol is present yields of 70 per cent should readily be obtained.
2. During the diazotization of the [aniline](#) the temperature must be kept at 0–5°. The amount of ice stated is usually enough for this, but if not, more must be added.
3. The stirring must be very uniform and vigorous during the addition of the [benzenediazonium chloride](#) solution to the α -naphthol; otherwise the precipitate collects in gummy balls. If properly carried out, the operation produces a fine red precipitate which filters easily and is not at all gummy. A more powerful motor than that ordinarily used is required for effective stirring.
4. The temperature at which the coupling takes place and the mixture is allowed to stand has a great influence on the amount of disazo compound formed, as much as 120 g. being produced if no external cooling is provided.
5. The reduction with [hydrosulfite](#) may be carried out in an atmosphere of illuminating gas or [hydrogen sulfide](#). The first precipitate of the free [aminophenol](#) is a little lighter in color when prepared in an inert atmosphere, but the final [aminonaphthol hydrochloride](#) has the usual light purple color.
6. If too much [hydrochloric acid](#) is added in the precipitation of the free [aminophenol](#), some will, of course, redissolve. The amount given above will give satisfactory results if the indicated quantities are adhered to.
7. The completeness of the precipitation should be tested by adding a little acid to one portion of the filtrate and a little [sodium carbonate](#) solution to another; no further precipitate should be produced in either case.
8. The [aminophenol hydrochloride](#) can be further purified by dissolving in hot water, cooling, and adding concentrated [hydrochloric acid](#). It crystallizes in beautiful crystals, but the light violet color is very difficult to remove.
9. A yield of 85–90 per cent is obtainable when the best grade of α -naphthol is used. In this case it is suggested that the alkali-insoluble precipitate from the [benzeneazo- \$\alpha\$ -naphthol](#) be not filtered as it is

very slight in amount and very difficult to filter. If the best grade of [α-naphthol](#) is used the amounts of water and [hydrochloric acid](#) to be used with the crude product should be multiplied by 1.3 (R. B. Whitney, private communication).

3. Discussion

1,4-Aminonaphthol can be prepared by the reduction of 1,4-nitronaphthol by [tin](#) and [hydrochloric acid](#),¹ and by the action of [phenylhydrazine](#) on 1,4-nitrosonaphthol.² The more usual preparative method has been to start with [α-naphthol orange](#) (Orange I) and reduce it with [stannous chloride](#).³ Orange I has also been reduced with [sodium hydrosulfite](#), using [stannous chloride](#) as an antioxidant in preparing and crystallizing the amine hydrochloride.⁴ The procedure described above makes possible the use of crude, technical [α-naphthol](#).

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 162](#)
- [Org. Syn. Coll. Vol. 2, 39](#)

References and Notes

1. Liebermann, *Ann.* **183**, 247 (1876).
2. Plancher, *Gazz. chim. ital.* **25** (2), 393 (1895) [*Chem. Zentr.* I, 436 (1896)].
3. Seidel, *Ber.* **25**, 423 (1892); Russig, *J. prakt. Chem.* (2) **62**, 31 (1900); Liebermann and Jacobson, *Ann.* **211**, 61 (1882).
4. Fieser and Fieser, *J. Am. Chem. Soc.* **57**, 491 (1935); *Org. Syn.* **17**, 9.

Appendix

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

1,4-Aminonaphthol hydrochloride

2,4-disazo derivative

benzeazo-β-naphthol

1,4-Aminonaphthol

1,4-nitronaphthol

1,4-nitrosonaphthol

α-naphthol orange

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

[aniline](#) (62-53-3)

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

hydrogen sulfide (7783-06-4)
sodium carbonate (497-19-8)
sulfur dioxide (7446-09-5)
1-Naphthol, 4-amino-, hydrochloride (5959-56-8)
 α -naphthol,
naphthol (90-15-3)
benzenediazonium chloride
aniline hydrochloride (142-04-1)
sodium nitrite (7632-00-0)
nitrous acid (7782-77-6)
nitrite (14797-65-0)
benzeneazo- α -naphthol
sodium hydrosulfite (7775-14-6)
aminonaphthol
aminonaphtholhydrochloride,
aminonaphthol hydrochloride (41772-23-0)
 β -naphthol (135-19-3)
hydrosulfite
aminophenol (95-55-6)
aminophenol hydrochloride (51-19-4)
tin (7440-31-5)
Phenylhydrazine (100-63-0)
stannous chloride