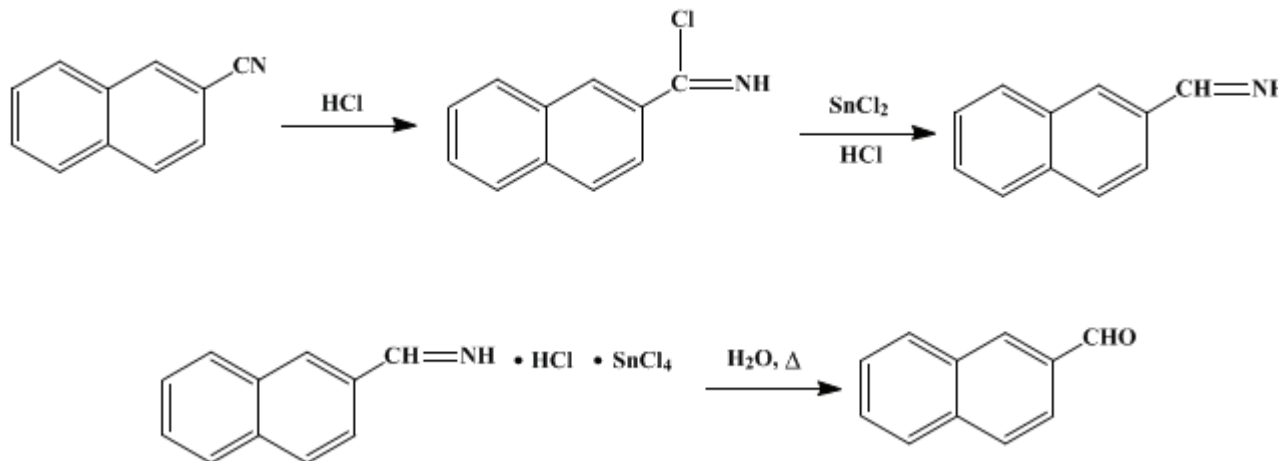


β -NAPHTHALDEHYDE

[2-Naphthaldehyde]

[I. METHOD A]



Submitted by Jonathan W. Williams
Checked by C. F. H. Allen and J. VanAllan.

1. Procedure

In a 2-l. three-necked round-bottomed flask, provided with a mechanical stirrer, a reflux condenser carrying a drying tube, and an inlet tube reaching nearly to the bottom of the flask, are placed 76 g. (0.4 mole) of anhydrous **stannous chloride** (Note 1) and 400 ml. of anhydrous **ether**. The mixture is then saturated with dry **hydrogen chloride**, while it is slowly stirred; this requires 2.5–3 hours, during which time the **stannous chloride** forms a viscous lower layer.

The inlet tube is replaced by a dropping funnel, and a solution of 30.6 g. (0.2 mole) of β -**naphtho-nitrile**, m.p. 60–62° (Note 2), in 200 ml. of dry **ether** is added rapidly. **Hydrogen chloride** is again passed into the mixture until it is saturated, and the mixture is then stirred rapidly for 1 hour and allowed to stand overnight while the yellow aldimine-stannichloride separates completely.

The ethereal solution is decanted, and the solid is rinsed with two 100-ml. portions of **ether**. The solid is transferred to a 5-l. flask fitted for steam distillation and immersed in an oil bath, the temperature of which is maintained at 110–120° (Note 3). Dry steam is passed through the mixture (Note 4) until the aldehyde is completely removed; this requires 8–10 hours, and 8–10 l. of distillate is collected.

The white solid is filtered and allowed to dry in the air; it amounts to 23–25 g. (73–80%) and melts at 53–54°. For further purification, it is distilled under reduced pressure (Note 5); the water-clear distillate (b.p. 156–158°/15 mm.) is poured into a mortar while hot and is pulverized when cool. The recovery is 93–95%, and the melting point is 57–58°.

2. Notes

1. The success of this type of reaction depends on the quality of the catalyst. The most active and dependable form of anhydrous **stannous chloride**¹ is prepared as follows: In a 600-ml. beaker is placed 204 g. (189 ml., 2 moles) of **acetic anhydride** (99–100%) and, while the liquid is stirred by hand, 226 g. (1 mole) of commercial C.P. crystalline **stannous chloride dihydrate** is added. This operation should be performed in a hood, for the heat of the reaction is sufficient to cause the **acetic anhydride** to boil. After

about 1.5 hours, the anhydrous **stannous chloride** is filtered on a large Büchner funnel, rinsed with two 50-ml. portions of dry **ether**, and dried overnight in a vacuum desiccator. The yield is quantitative (189 g.). The product may be kept in a tightly closed bottle until it is wanted. The product secured by dehydrating crystalline **stannous chloride** in an oil bath at 195–200° is satisfactory in many instances but is not dependable.

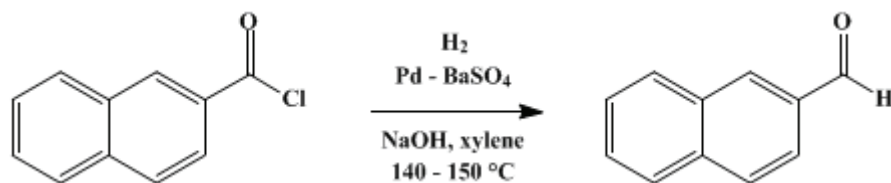
2. **β -Naphthonitrile** is prepared by the procedure described under *o*-Tolunitrile, in *Org. Syntheses Coll. Vol. 1*, 514 (1941).

3. The use of dry, slightly superheated steam reduces the time of distillation but is not essential.

4. A superheater obtained from the Fisher Scientific Company was used. It was preceded by the usual steam trap to remove the condensed water. The thermometer in the superheater recorded 260°.

5. It is convenient to combine the material from several runs.

[II. METHOD B]



Submitted by E. B. Hershberg and James Cason.

Checked by Nathan L. Drake, Harry D. Anspson, and Ralph Mozingo.

1. Procedure

A 500-ml. three-necked flask, *equipped with ground joints*, is fitted with a mercury-sealed stirrer (**Note 1**), a reflux condenser, and a gas-inlet tube extending to a point just above the stirrer. In the flask are placed 57 g. (0.30 mole) of **β -naphthoyl chloride** (**Note 2**), 200 ml. of **xylene** (**Note 3**), 6 g. of **palladium-barium sulfate** catalyst (p. 685), and 0.6 ml. of stock poison solution (**Note 4**). The top of the condenser is connected by a rubber tube to a 6-mm. glass tube extending to the bottom of a 500-ml. Erlenmeyer flask containing 400 ml. of distilled water and a few drops of **phenolphthalein** indicator solution. A buret containing approximately 5 *N* **sodium hydroxide** solution (prepared by dissolving 20.5 g. of analytical reagent **sodium hydroxide** in water and diluting to 100 ml.) is arranged for delivery into this flask, which for safety should be placed at least 2 ft. away from any flame. Commercial electrolytic **hydrogen** is passed from a cylinder directly into the reaction flask at such a rate that 100–300 bubbles per minute emerge in the Erlenmeyer flask.

After the air in the reaction flask has been displaced by **hydrogen**, the flask is heated in an oil bath at 140–150°, the stirrer is started (**Note 5**), and 1 ml. of alkali is run into the Erlenmeyer flask. The course of the reaction is followed by the rate of **hydrogen chloride** evolution. The first 5 ml. of alkali should be neutralized in 12–15 minutes, and the reaction should be complete in approximately 3 hours. About 92% of the theoretical amount of **hydrogen chloride** (equivalent to 55 ml. of 5 *N* **sodium hydroxide** solution) is recovered. The end of the reaction is evidenced by a rather abrupt cessation of **hydrogen chloride** evolution, and the reaction is discontinued at this point.

The flask is cooled, 1–2 g. of Norit added with stirring, and the solution filtered with suction through a hardened filter paper (**Note 6**). The **xylene** is removed from the nearly colorless filtrate by flash distillation under diminished pressure. For this purpose, a 125-ml. modified Claisen flask is arranged for vacuum distillation, the usual capillary being replaced by a separatory funnel whose stem extends to the bottom of the flask. The flask is heated in an oil bath at 90–100° and the solution added from the funnel as rapidly as possible without causing accumulation of **xylene** in the distilling flask. After all the solution has been added, the separatory funnel is replaced by a capillary and the bath temperature is raised. After a small fore-run consisting mostly of **naphthalene**, the **β -naphthaldehyde** distils at 147–149°/11 mm. (bath temperature 170–180°), leaving a small non-volatile residue. In this way, 34.5–38 g. (74–81%) of white aldehyde, m.p. 59–60°, is obtained (**Note 7**).

2. Notes

1. A Hershberg [tantalum](#) or [platinum](#) wire stirrer whose shaft runs in a ball bearing is convenient, but an ordinary all-glass stirrer may be used. The stirrer must be capable of running at a high speed, for the rate of reaction is dependent to a high degree on the speed of stirring. It is also extremely important that the stirrer be carefully lined up so that there is a minimum of splashing of [mercury](#) in the seal. If [mercury](#) works down into the flask, the reaction will not proceed properly ([Note 5](#)).
2. [β-Naphthoyl chloride](#) is conveniently prepared from [β-naphthoic acid](#) and [phosphorus pentachloride](#). A mixture of 57.4 g. (0.33 mole) of acid and 69 g. (0.33 mole) of [phosphorus pentachloride](#) in a 250-ml. modified Claisen distilling flask is warmed on a steam bath in a hood. As soon as the vigorous reaction sets in, the flask is removed from the steam bath until the rapid evolution of [hydrogen chloride](#) has moderated, then warmed on the steam bath for 30 minutes. After removal of the [phosphorus oxychloride](#) at diminished pressure, using a water pump, the acid [chloride](#) is distilled. The fraction boiling at 160–162°/11 mm. (bath temperature 170–180°) weighs 57–60 g. (90–95%) and melts at 51–52°. The distillation should be carefully conducted, and a quite colorless product should result.
3. One liter of technical [xylene](#) is refluxed overnight with 2 g. of [sodium](#), distilled, and stored over [sodium](#).
4. The [quinoline-sulfur](#) poison of Rosenmund and Zetsche² is prepared by refluxing 1 g. of [sulfur](#) with 6 g. of [quinoline](#) for 5 hours and diluting the resultant dark brown liquid to 70 ml. with the purified [xylene](#). The literature on the Rosenmund reduction contains many conflicting reports concerning the necessity for a catalyst poison; however, the work of Zetsche and collaborators^{3,4} indicates that the purity of the solvent is the determining factor. These workers found that by using technical [xylene](#) without added poison a good yield of aldehyde could usually be obtained but after the [xylene](#) had been purified by distilling over anhydrous [aluminum chloride](#) practically no aldehyde was obtained under the same conditions. Instead, products arising from further reduction of the aldehyde were obtained. In view of these results the use of a poison is recommended in order to ensure controlled conditions. The submitters claim that the use of twice the ratio of poison specified has no effect except slowing up the reaction; the yield and quality of the product remain the same.
5. The rapid rate of stirring desirable for maximum reaction rate often causes spraying of fine droplets of [mercury](#) from the seal. This can be prevented by a layer of paraffin oil over the [mercury](#). It is important for the gas-inlet tube to extend below the surface of the stirred liquid, for absorption of [hydrogen](#) occurs chiefly at the rapidly agitated surface.
6. The [palladium](#) may be recovered from used catalyst by ignition and solution in aqua regia.⁵
7. According to the submitters, this reaction is quite satisfactory on a small scale and can be used with other acid chlorides. In a 0.05-mole run carried out in the same manner, an 83% yield of [β-naphthaldehyde](#) was obtained. [1-Acetoxy-3-naphthaldehyde](#), m.p. 112–114°, was obtained in 70% yield from 0.85 g. of the corresponding acid chloride. [Methyl β-formylpropionate](#), b.p. 69–70°/14 mm., was also obtained in 65% yield from the acid chloride; reduction proceeds rapidly at 110° in this case.

3. Discussion

[β-Naphthaldehyde](#) has been prepared from [β-chloromethylnaphthalene](#) by the use of [hexamethylenetetramine](#) in [ethanol](#),⁶ or by oxidation with [lead nitrate](#);⁷ from [β-bromomethylnaphthalene](#) by the use of [hexamethylenetetramine](#) in [ethanol](#)⁸ or in [acetic acid](#),⁹ or by oxidation with [lead nitrate](#);⁷ by distillation of a mixture of [calcium formate](#) and [calcium β-naphthoate](#);^{10,11} by reduction of [β-naphthoic acid](#) with [sodium amalgam](#);¹² from [β-naphthylcarbinol](#) by oxidation with [chromic acid](#);¹³ from [β-naphthylglyoxylic acid anil](#);¹⁴ from [β-naphthylmagnesium iodide](#) and [methyl orthoformate](#);¹⁵ from [β-naphthylmagnesium bromide](#) and [ethoxymethylaniline](#)¹⁶ or orthoformic ester;^{14,17} by treatment of [β-naphthylmagnesium bromide](#) with [carbon disulfide](#), followed by conversion of the dithioacid to a semicarbazone and hydrolysis;¹⁸ from [β-naphthonitrile](#) by Stephen reduction;^{19,20} from [β-naphthoyl chloride](#) by Rosenmund reduction;^{3,21,22} and from [2-methylnaphthalene](#) by oxidation with [selenium dioxide](#).²³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 549](#)

- Org. Syn. Coll. Vol. 3, 601
- Org. Syn. Coll. Vol. 3, 818
- Org. Syn. Coll. Vol. 4, 444

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

semicarbazone

aldimine-stannichloride

β -naphthylcarbinol

β -naphthylglyoxylic acid anil

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

acetic anhydride (108-24-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

stannous chloride

sulfur (7704-34-9)

mercury (7439-97-6)

platinum (7440-06-4)

Phosphorus Oxychloride (21295-50-1)

aluminum chloride (3495-54-3)

selenium dioxide (7446-08-4)

sodium (13966-32-0)

lead nitrate (10099-74-8)

palladium (7440-05-3)

chromic acid (7738-94-5)

carbon disulfide (75-15-0)

Naphthalene (91-20-3)

xylene (106-42-3)

Quinoline (91-22-5)

hexamethylenetetramine (100-97-0)

phenolphthalein (77-09-8)

o-Tolunitrile (529-19-1)

chloride

stannous chloride dihydrate (10025-69-1)

tantalum (7440-25-7)

calcium formate (544-17-2)

β -Naphthoic acid (93-09-4)

β -naphthonitrile (613-46-7)

2-methylnaphthalene (91-57-6)

palladium-barium sulfate

β -naphthoyl chloride (2243-83-6)

β -Naphthaldehyde,
2-Naphthaldehyde (66-99-9)

quinoline-sulfur

1-Acetoxy-3-naphthaldehyde

Methyl β -formylpropionate (13865-19-5)

β -chloromethylnaphthalene (2506-41-4)

β -bromomethylnaphthalene (939-26-4)

calcium β -naphthoate

β -naphthylmagnesium iodide

methyl orthoformate

β -naphthylmagnesium bromide

ethoxymethylaniline