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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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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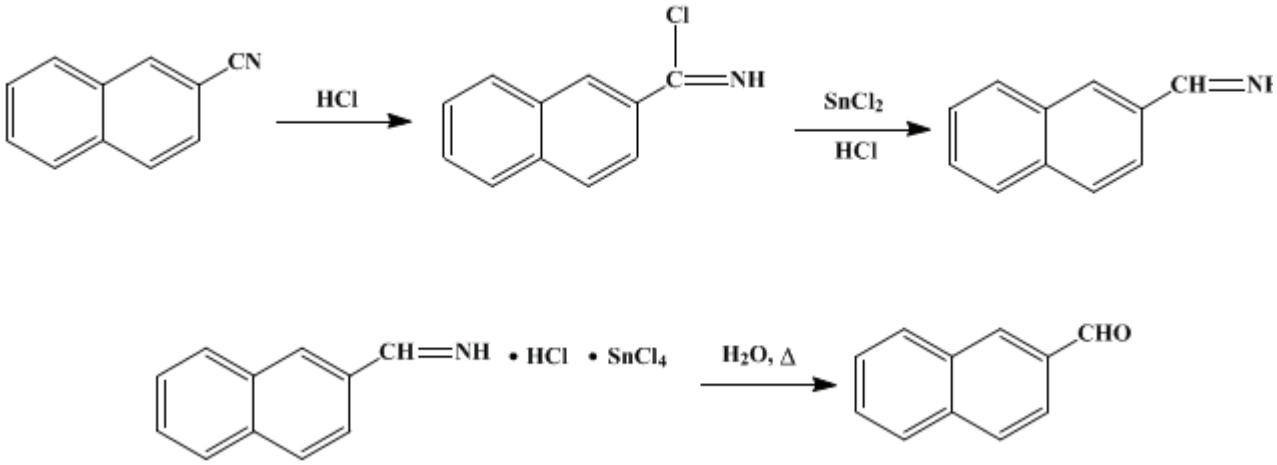
Organic Syntheses, Coll. Vol. 3, p.626 (1955); Vol. 23, p.63 (1943).

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-naphthonitrile, 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.

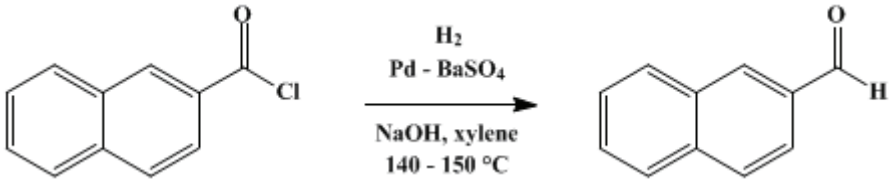
2. β-Naphthonitrile is prepared by the procedure described under *o*-Tolunitrile, in *Org. Syntheses* Coll. Vol. 1, 514 (1941).

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. Anspon, 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 Zetzsche[2] 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 Zetzsche 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