



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.

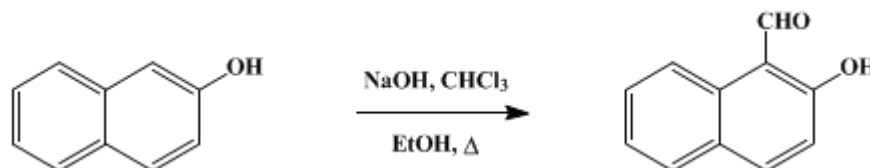
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.463 (1955); Vol. 22, p.63 (1942).

2-HYDROXY-1-NAPHTHALDEHYDE

[1-Naphthaldehyde, 2-hydroxy-]



Submitted by Alfred Russell and Luther B. Lockhart.
Checked by W. E. Bachmann and Charles E. Maxwell.

1. Procedure

In a 2-l. three-necked round-bottomed flask (Note 1) fitted with a 40-in. reflux condenser, a mercury-sealed stirrer, and a dropping funnel are placed 100 g. (0.69 mole) of β -naphthol and 300 g. of 95% ethanol. The stirrer is started, and a solution of 200 g. (5 moles) of sodium hydroxide in 415 g. of water is rapidly added.

The resulting solution is heated to 70–80° on a steam bath, and the dropwise addition of chloroform is started. After the reaction begins (Note 2), further heating is unnecessary. A total of 131 g. (1.1 moles) of chloroform is added at such a rate that gentle refluxing is maintained (Note 3). Near the end of the addition the sodium salt of the phenolic aldehyde separates. Stirring is continued for 1 hour after all the chloroform has been added.

The ethanol and excess chloroform are removed by distillation from a steam bath. Hydrochloric acid (sp. gr. 1.18) is added dropwise to the residue, with good stirring, until the contents of the flask are acid to Congo red paper (Note 4). The dark oil that separates is mixed with a considerable amount of sodium chloride. Sufficient water to dissolve the salt is added, and the oil is separated and washed several times with hot water. By distillation of the oil under reduced pressure there is obtained 87.5–93.7 g. of a slightly colored distillate which boils at 163–166° at 8 mm. (Note 5) and which solidifies on cooling. Recrystallization of the solid from 75 ml. of ethanol yields 45.2–57.5 g. (38–48%) of pure 2-hydroxy-1-naphthaldehyde, melting at 79–80°.

2. Notes

1. The submitters employed a 5-l. flask for a run four times this size. They obtained the same percentage yield of product.
2. The beginning of the reaction is indicated by the formation of a deep blue color.
3. The chloroform is added over a period of 1 to 1.5 hours.
4. About 175 ml. of hydrochloric acid is required to neutralize the excess sodium hydroxide and to liberate the phenolic aldehyde from its sodium salt.
5. The boiling range of the aldehyde is 177–180°/20 mm. The lower pressure is preferable to avoid decomposition. The checkers found a boiling point of 139–142°/4 mm. The color of the distillate varies in different runs; it may be green, pink, or amber.

3. Discussion

2-Hydroxy-1-naphthaldehyde has been prepared from β -naphthol, zinc chloride, and hydrogen cyanide;¹ from β -naphthol, zinc cyanide, and anhydrous hydrogen chloride;² from β -naphthol, chloroform, and sodium hydroxide (Reimer-Tiemann reaction);^{3,4} from β -naphthol and hexamethylene tetramine in glycerin-boric acid, followed by hydrolysis;⁵ and by hydrolysis of 2-hydroxynaphthaldehyde anil,⁶ prepared in turn from 2-hydroxydithionaphthoic acid.⁷

References and Notes

1. Gattermann and von Horlacher, *Ber.*, **32**, 285 (1899).
 2. Adams and Levine, *J. Am. Chem. Soc.*, **45**, 2373 (1923).
 3. Fosse, *Bull. soc. chim. France*, (3) **25**, 373 (1901).
 4. Kolesnikov, Korshak, and Krakovnaya, *Zhur. Obshchei Khim.*, **21**, 397 (1951) [*C. A.*, **45**, 7553 (1951)].
 5. Duff, *J. Chem. Soc.*, **1941**, 547.
 6. Brit. pat. 563,747 [*C. A.*, **40**, 3141 (1946)].
 7. Brit. pat. 563,942 [*C. A.*, **40**, 3141 (1946)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sodium salt of the phenolic aldehyde

2-hydroxynaphthaldehyde anil

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium chloride (7647-14-5)

hydrogen cyanide (74-90-8)

β -naphthol (135-19-3)

zinc chloride (7646-85-7)

phenolic aldehyde (90-02-8)

hexamethylene tetramine (100-97-0)

2-Hydroxy-1-naphthaldehyde,
1-Naphthaldehyde, 2-hydroxy- (708-06-5)

glycerin-boric acid

2-hydroxydithionaphthoic acid

zinc cyanide (557-21-1)

