



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.

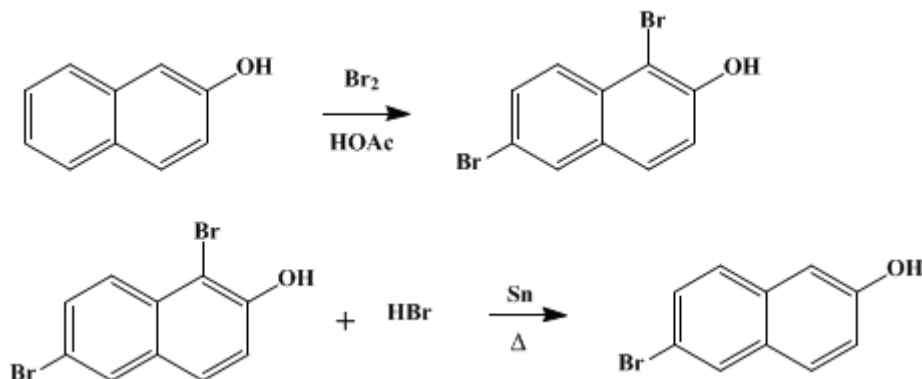
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.132 (1955); Vol. 20, p.18 (1940).

6-BROMO-2-NAPHTHOL

[2-Naphthol, 6-bromo-]



Submitted by C. Frederick Koelsch

Checked by W. E. Bachmann and S. Kushner.

1. Procedure

In a 3-l. round-bottomed flask fitted with a dropping funnel and a reflux condenser ([Note 1](#)) are placed 144 g. (1 mole) of β -naphthol and 400 ml. of glacial acetic acid. Through the dropping funnel is then added a solution of 320 g. (2 moles) of bromine in 100 ml. of acetic acid. The flask is shaken gently during the addition, which requires 15–30 minutes. The β -naphthol dissolves during this period, and heat is evolved; the mixture is cooled somewhat towards the end of the addition to avoid excessive loss of hydrogen bromide. One hundred milliliters of water is then added, and the mixture is heated to boiling. It is then cooled to 100°, 25 g. of mossy tin is added ([Note 2](#)), and boiling is continued until the metal is dissolved. A second portion of 25 g. of tin is then added and dissolved by boiling, and finally a third portion of 100 g. (a total of 150 g., 1.27 gram atoms) of tin is introduced. The mixture is boiled for 3 hours, cooled to 50°, and filtered with suction. The crystalline tin salts which are thus removed are washed on the funnel with 100 ml. of cold acetic acid, the washings being added to the main portion of the filtrate.

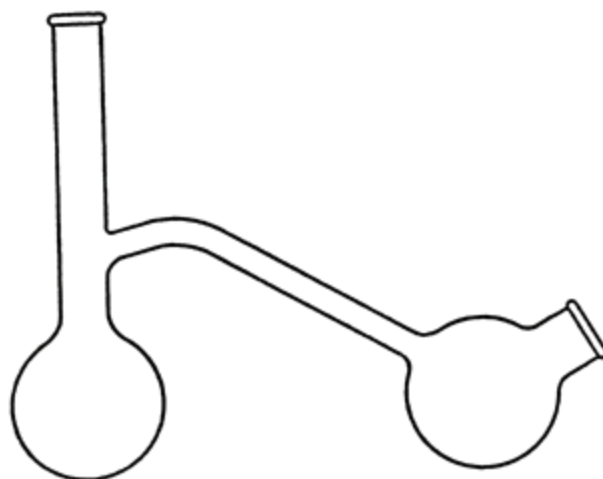
This filtrate is stirred into 3 l. of cold water; the 6-bromo-2-naphthol which is precipitated is filtered with suction, removed from the funnel, and washed by stirring with 1 l. of cold water. After filtering again and drying at 100° there is obtained 214–223 g. (96–100%) of 6-bromo-2-naphthol. This crude product, which is pink and melts at 123–127°, contains some tin but is pure enough for most purposes.

A white product is obtained by vacuum distillation followed by crystallization of the crude product. Twenty-five grams of the crude substance on distillation ([Note 3](#)) gives 20 to 24 g. of distillate boiling at 200–205°/20 mm., and when this is crystallized from a mixture of 75 ml. of acetic acid and 150 ml. of water it gives 17.5 to 22.5 g. of 6-bromo-2-naphthol which melts at 127–129°.

2. Notes

1. An all-glass apparatus is of considerable advantage. If this is not available, the cork is covered with lead foil.
2. The reflux condenser is removed in order to add the tin, but it should be held in readiness so that it can be replaced quickly. The first two portions of tin react vigorously, and solution of the metal is accompanied by the evolution of hydrogen and the loss of some hydrogen bromide.
3. For the distillation a sausage flask or two-bulb flask ([Fig. 6](#)) is employed.

Fig. 6.



3. Discussion

6-Bromo-2-naphthol has been prepared by the reduction of 1,6-dibromo-2-naphthol with hydriodic acid,² with tin and hydrochloric acid,³ or with stannous chloride and hydrochloric acid in aqueous alcohol³ or in aqueous acetic acid.⁴ It has also been obtained by the bromination of 2-naphthol with pyridinium bromide perbromide.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 828
- Org. Syn. Coll. Vol. 5, 918
- Org. Syn. Coll. Vol. 6, 34

References and Notes

1. Fieser, *Experiments in Organic Chemistry*, p. 246, D. C. Heath & Company, Boston, 1935.
 2. Armstrong, *Chem. News*, **74**, 302 (1897).
 3. Franzen and Staubel, *J. prakt. Chem.*, (2) **103**, 369 (1922); Fries and Schimmelschmidt, *Ber.*, **58**, 2840 (1925).
 4. Fries and Schimmelschmidt, *Ann.*, **484**, 293 (1930).
 5. Vona and Merker, *J. Org. Chem.*, **14**, 1048 (1949).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

pyridinium bromide perbromide

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

hydrogen (1333-74-0)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

β -naphthol,
2-naphthol (135-19-3)

tin (7440-31-5)

stannous chloride

hydriodic acid (10034-85-2)

6-Bromo-2-naphthol,
2-Naphthol, 6-bromo- (15231-91-1)

1,6-dibromo-2-naphthol (16239-18-2)