



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](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.

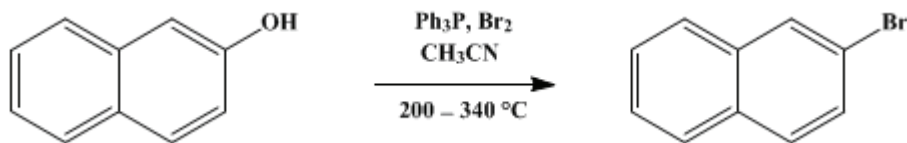
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 5, p.142 (1973); Vol. 49, p.6 (1969).*

## 2-BROMONAPHTHALENE

[Naphthalene, 2-bromo-]



Submitted by J. P. Schaefer, Jerry Higgins, and P. K. Shenoy<sup>1</sup>.

Checked by James P. Nelson, Wayland E. Noland, and William E. Parham.

### 1. Procedure

A 500 ml., three-necked, round-bottomed flask is equipped with a Trubore stirrer, a pressure-compensating dropping funnel, and a reflux condenser with drying tube. The flask is charged with 144 g. of triphenylphosphine (0.55 mole) (Note 1) and 125 ml. of acetonitrile (Note 2) and (Note 3). The solution is stirred and cooled in an ice bath and 88 g. of bromine is added dropwise over a period of 20–30 minutes (Note 4). After the addition of the bromine (Note 5) is complete, the ice bath is removed and 72 g. (0.50 mole) of  $\beta$ -naphthol (Note 6) in 100 ml. of acetonitrile (Note 7) is added in one portion and the reaction mixture is heated to 60–70° for at least 30 minutes (Note 8). The flask is now fitted for a simple distillation, stirring is discontinued, and the acetonitrile is distilled (Note 9) under aspirator pressure until the oil bath temperature reaches 110° (Note 10). After all the acetonitrile has been removed, the condenser is replaced by a short, large glass tube (Note 11) connected to a 500-ml. flask half-filled with water, and the oil bath is replaced by a Wood's metal bath. The bath temperature is now raised to 200–220° and kept at this temperature until all the solid has melted (Note 12). The mixture is stirred and the bath temperature is raised to 340° (Note 13) and held at this temperature until evolution of hydrogen bromide ceases (approximately 20–30 minutes). The Wood's metal bath is removed and the reaction mixture is cooled to approximately 100° and then poured into a 1-l. beaker and cooled to room temperature. Pentane (300 ml.) (Note 14) is added and the solid is broken into a fine precipitate (Note 15). The solid is filtered by suction and washed thoroughly with two 300-ml. portions of pentane. The pentane filtrates are combined, washed with 200 ml. of 20% sodium hydroxide, and dried over anhydrous magnesium sulfate. The pentane extract is then passed through a 25 mm. diameter column filled to 35 cm. in depth with alumina; distillation of the pentane at reduced pressure gives 72–81 g. (70–78%) (Note 16) of 2-bromonaphthalene, a white solid melting at 45–50° (reported:<sup>2</sup> 55–56.4°) (Note 17), (Note 18).

### 2. Notes

1. Triphenylphosphine was obtained from M and T Chemicals Inc. and was used without further purification.
2. The acetonitrile was *cautiously* distilled from phosphorus pentoxide. The solid phosphorus pentoxide may cause bumping during the distillation of the acetonitrile. This can be avoided if the solution is stirred during the distillation.
3. The triphenylphosphine is only partially dissolved.
4. The temperature is kept below 40° and the reaction mixture thoroughly stirred during this addition.
5. If a small amount of free bromine remains, as evidenced by color, then a sufficient amount of triphenylphosphine is added to take up the bromine.
6. Practical grade  $\beta$ -naphthol was obtained from Matheson Coleman and Bell and distilled at atmospheric pressure before use.
7. Warming the acetonitrile is necessary to dissolve the  $\beta$ -naphthol.
8. All the precipitate dissolves at this point. The checkers heated the mixture for 2 hours. The solids appeared to dissolve; then there was some reprecipitation. All solids had not dissolved after 2 hours at 70°.

9. The checkers encountered severe bumping during distillation of the [acetonitrile](#). The [acetonitrile](#) may be removed with only moderate bumping if no external heat is applied.
10. The checkers did not remove all the [acetonitrile](#) at 110°, a factor which contributed to foaming later ([Note 12](#)).
11. If a tube smaller than ½ inch in diameter is used, it may become plugged later in the reaction.
12. If temperature is higher than 220°, initial foaming may become troublesome. The checkers heated the solid to 240–270°, since melting did not occur at 200–220°; foaming was encountered.
13. Evolution of [hydrogen bromide](#) begins at about 280°.
14. The checkers used petroleum ether (b.p. 65–67°).
15. The checkers obtained a somewhat tarry precipitate.
16. The submitters obtained 85–87 g. (82–86% yield).
17. The checkers' product retained solvent. The product was heated for a short period at 120° (20 mm.) and a crystalline solid, free of solvent, was obtained.
18. Purity was checked by analytical vapor phase chromatography (98–99%). This product can be used for most reactions without further purification. If further purification is desired, [2-bromonaphthalene](#) can be recrystallized from aqueous [methanol](#) (95% recovery) to give a product melting at 53–55°.

### 3. Discussion

[2-Bromonaphthalene](#) has been prepared from [2-aminonaphthalene](#) by the reaction of [mercuric bromide](#) with the [diazonaphthalene](#).<sup>2,3</sup> The reaction described in this preparation appears to be fairly general and provides a useful alternative method for introducing [bromine](#) into the aromatic nucleus. Using conditions similar to those outlined, the following have been prepared from the corresponding aryl alcohols:<sup>4,5</sup> [α-bromonaphthalene](#) (72%), [3-bromopyridine](#) (76%), [2-bromopyridine](#) (61%), [8-bromoquinoline](#) (48%), [o-bromotoluene](#) (72%), [p-chlorobromobenzene](#) (90%), [p-nitrobromobenzene](#) (60%), and [p-methoxybromobenzene](#) (59%). The use of the triphenylphosphinehalogen complex to convert alcohols to alkylhalides is described elsewhere in this series.<sup>6</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 10, 349](#)

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### References and Notes

1. Department of Chemistry, The University of Arizona, Tucson, Arizona.
2. M. S. Newman and P. H. Wise, *J. Am. Chem. Soc.*, **63**, 2847 (1941).
3. H. W. Schwechten, *Ber.*, **65**, 1605 (1932).
4. J. P. Schaefer and J. Higgins, *J. Org. Chem.*, **32**, 1607 (1967).
5. G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).
6. J. P. Schaefer, J. G. Higgins, and P. K. Shenoy, *this volume*, p. 249.

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### Appendix

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

petroleum ether

[methanol](#) (67-56-1)

[acetonitrile](#) (75-05-8)

sodium hydroxide (1310-73-2)  
hydrogen bromide (10035-10-6)  
bromine (7726-95-6)  
 $\beta$ -naphthol (135-19-3)  
 $\alpha$ -Bromonaphthalene (90-11-9)  
Naphthalene, 2-bromo-,  
2-Bromonaphthalene (580-13-2)  
Pentane (109-66-0)  
magnesium sulfate (7487-88-9)  
mercuric bromide (7789-47-1)  
o-Bromotoluene (95-46-5)  
2-Bromopyridine (109-04-6)  
3-bromopyridine (626-55-1)  
triphenylphosphine (603-35-0)  
2-aminonaphthalene (91-59-8)  
diazonaphthalene  
8-bromoquinoline (16567-18-3)  
p-methoxybromobenzene (104-92-7)  
p-chlorobromobenzene (106-39-8)  
phosphorus pentoxide (1314-56-3)  
p-nitrobromobenzene (586-78-7)