



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.

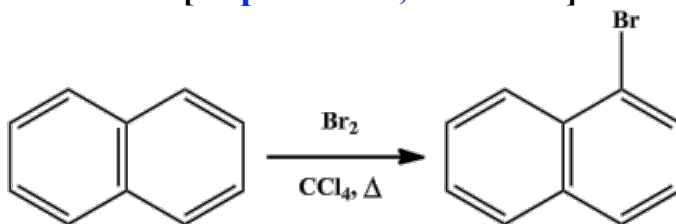
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 1, p. 121 (1941); Vol. 1, p.35 (1921).*

## **$\alpha$ -BROMONAPHTHALENE**

**[Naphthalene, 1-bromo-]**



Submitted by H. T. Clarke and M. R. Brethen.

Checked by J. B. Conant and G. W. Wheland.

### **1. Procedure**

In a 2-l. flask are placed 512 g. (4 moles) of [naphthalene](#) and 275 g. (170 cc.) of [carbon tetrachloride](#). The flask is equipped with a stirrer, an efficient reflux condenser, and a dropping funnel, the stem of which extends below the level of the liquid. From the top of the reflux condenser a tube leads to a water trap similar to that described in [Fig. 7 on p. 97](#). The mixture is warmed on a steam bath to gentle boiling, and 707 g. (220 cc., 4.4 moles) of [bromine](#) is run in at such a rate that practically none of it is carried over with the [hydrogen bromide](#) into the trap. This requires from twelve to fifteen hours, during which time the mixture is gently warmed on the steam bath, with continual stirring, until the evolution of [hydrogen bromide](#) ceases (about six hours). The mixture is now distilled from the steam bath under slightly reduced pressure (using a condenser) until free of [carbon tetrachloride](#); the residue is mixed with 20–30 g. of powdered or granulated [sodium hydroxide](#) and stirred at 90–100° for four hours ([Note 1](#)). The liquid is transferred to a flask for fractional distillation and distilled under reduced pressure. The forerun contains a considerable proportion of unchanged [naphthalene](#), the bulk of which is removed by chilling and filtering with suction; the main fraction, consisting of [bromonaphthalene](#), passes over at 132–135°/12 mm. (145–148°/20 mm.), and a high-boiling fraction, consisting of [dibromonaphthalene](#), is collected. The intermediate fractions and the filtrates from the foreruns are systematically redistilled; in this way 600–620 g. of colorless  [\$\alpha\$ -bromonaphthalene](#) (72–75 per cent of the theoretical amount) and about 30 g. of a mixture of dibromonaphthalenes (m.p., about 60°) are obtained.

### **2. Notes**

1. If this treatment with [sodium hydroxide](#) is omitted, the final product contains impurities which gradually give off [hydrogen bromide](#).

### **3. Discussion**

[\$\alpha\$ -Bromonaphthalene](#) can be prepared by the action of [bromine](#) upon [naphthalene](#) without a solvent<sup>1</sup> and in [carbon disulfide](#);<sup>2</sup> by treating a suspension of [naphthalene](#) in a solution of [bromine](#) in alkali with [hydrochloric acid](#);<sup>3</sup> and by treating a suspension of [naphthalene](#) in warm water with [bromine](#).<sup>4</sup> The procedure described has been found to be more convenient and to give considerably better yields than that reported previously.<sup>4</sup> An essentially similar procedure has been described.<sup>5</sup> The method in which a suspension of [naphthalene](#) in alkaline [hypobromite](#) solution is treated with [hydrochloric acid](#) in aqueous solution<sup>3</sup> was found to give a satisfactory yield, but it presented

considerable difficulties in the recovery of the [hydrobromic acid](#). [Iodine monobromide](#) has been used successfully to brominate [naphthalene](#).<sup>6</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 425](#)

## References and Notes

1. Laurent and Wahlforss, Z. Chem. 3 (1865).
2. Glaser, Ann. **135**, 40 (1865); Otto, Ann. **147**, 166 (1868).
3. Merz and Weith, Ber. **15**, 2721 (1882).
4. Clarke and Schram, Org. Syn. **1**, 35 (1921).
5. Blicke, J. Am. Chem. Soc. **49**, 2846 (1927).
6. Militzer, *ibid.* **60**, 257 (1938).

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

mixture of dibromonaphthalenes

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

HYDROBROMIC ACID,  
hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

carbon disulfide (75-15-0)

$\alpha$ -Bromonaphthalene,  
bromonaphthalene (90-11-9)

Naphthalene, 2-bromo- (580-13-2)

Naphthalene (91-20-3)

dibromonaphthalene  
hypobromite

Iodine monobromide (7789-33-5)