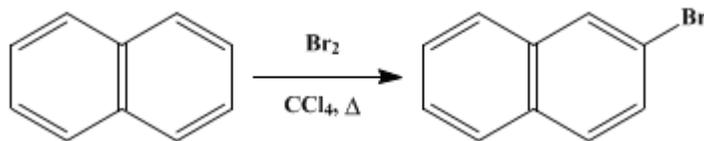


α -BROMONAPHTHALENE

[Naphthalene, 2-bromo-]



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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 α -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

α -Bromonaphthalene can be prepared by the action of bromine upon naphthalene without a solvent¹ and in carbon disulfide;² by treating a suspension of naphthalene in a solution of bromine in alkali with hydrochloric acid;³ and by treating a suspension of naphthalene in warm water with bromine.⁴ The procedure described has been found to be more convenient and to give considerably better yields than that reported previously.⁴ An essentially similar procedure has been described.⁵ The method in which a suspension of naphthalene in alkaline hypobromite solution is treated with hydrochloric acid in aqueous solution³ 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.⁶

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).
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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)

α -Bromonaphthalene,
bromonaphthalene (90-11-9)

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

Naphthalene (91-20-3)

dibromonaphthalene

hypobromite

Iodine monobromide (7789-33-5)