



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.

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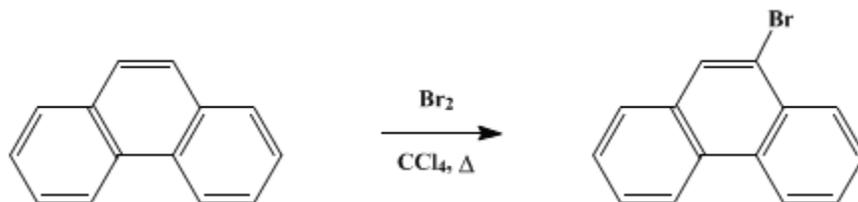
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.134 (1955); Vol. 28, p.19 (1948).

9-BROMOPHENANTHRENE

[Phenanthrene, 9-bromo-]



Submitted by Clinton A. Dornfeld, Joseph E. Callen, and George H. Coleman¹.
Checked by Robert E. Carnahan and Homer Adkins.

1. Procedure

A. *Purification of technical phenanthrene.* One and one-half kilograms of technical 90% phenanthrene is dissolved in 9 l. of ethanol in a 12-l. flask on a steam bath, and the hot solution is decanted from any insoluble material. The product crystallizes upon cooling of the solution. One kilogram of the crystallized product is dissolved in 2.2 l. of hot glacial acetic acid in a 5-l. three-necked flask provided with an efficient reflux condenser and a dropping funnel. To the boiling solution is gradually added 72 ml. of an aqueous solution containing 60 g. of chromic anhydride, and then 30 ml. of concentrated sulfuric acid is added slowly from the dropping funnel. The solution is refluxed for 15 minutes. The hot solution is then poured with vigorous stirring into 4.5 l. of water in a 12-l. round-bottomed flask. After cooling, the mixture is filtered, and the product is washed with water and air-dried. The product is distilled (Note 1) at 148–149°/1 mm. The distillate is recrystallized from ethanol to give 800–900 g. of nearly white phenanthrene, m.p. 98.7–99°.

B. *9-Bromophenanthrene.* One kilogram (5.6 moles) of pure phenanthrene (Note 2) is dissolved in 1 l. of dry carbon tetrachloride in a 5-l. three-necked flask. A 500-ml. dropping funnel, a reflux condenser (with tube to conduct evolved hydrogen bromide to the hood), and an efficient motor-driven sealed stirrer (Note 3) are attached. The mixture is heated at gentle reflux with stirring, and 900 g. (5.64 moles) of bromine is added from the dropping funnel over a period of about 3 hours. After stirring at gentle reflux for 2 additional hours, during which most of the remaining hydrogen bromide is evolved, the reaction mixture is placed in a Claisen flask and the solvent is distilled at a pressure of 10–30 mm. The flask containing the residue is then provided with a fine capillary inlet tube, a thermometer, and a 2-l. distilling flask as receiver. The impure 9-bromophenanthrene is distilled (Note 4), and the material boiling at 177–190°/2 mm. is collected. The yield is 1300–1360 g. (90–94%), m.p. 54–56° (Note 5) and (Note 6).

2. Notes

1. Since the melting point of phenanthrene is relatively close to its boiling point under the pressure of the distillation, it is necessary to employ an apparatus so constructed that the solidified distillate will not clog the outlet tube. The submitters used a 2-l. modified Claisen flask attached directly, with a 14-mm. glass tube, to a 2-l. round-bottomed flask. The checkers used a similar all-glass apparatus.
2. The checkers used from 100 to 250 g. of phenanthrene with corresponding reductions of other quantities specified in the procedure.
3. A glycerol-rubber tube seal made with Neoprene rather than natural rubber is very satisfactory.
4. The flask may be supported on a wire gauze and heated directly with a Fisher or Meker burner. A modified Claisen flask equipped with a short column is desirable, but an ordinary Claisen flask can be used if the heating is carefully controlled to prevent impure bromophenanthrene from splashing over. The oil pump should be protected with the usual Dry Ice trap and with a potassium hydroxide tower to absorb hydrogen bromide. Even in runs in which the carbon tetrachloride solution was washed successively with sodium bisulfite, sodium carbonate, and water, much hydrogen bromide was evolved

during distillation.

5. If the distillation is performed carefully the product is probably sufficiently pure for most purposes without recrystallization. 9-Bromophenanthrene may be recrystallized from ethanol (about 10 ml. per g.).

6. In runs of one-tenth the scale specified, the product obtained by the checkers had a melting point of 50–55° when yields above 90% were obtained. The yields were about 10% lower when 9-bromophenanthrene of melting point 54–56° was produced. The yield of recrystallized compound, melting at 65–66°, as obtained by the checkers, was 60% of the theoretical.

3. Discussion

The procedure for the purification of technical phenanthrene is that of W. E. Bachmann² with slight modification.

The procedure described for the preparation of 9-bromophenanthrene is an adaptation of that described by Henstock,³ who effected the bromination at various temperatures and in different solvents but gave little experimental detail. Other methods⁴ of preparation involve the formation and isolation of phenanthrene dibromide and its subsequent conversion to 9-bromophenanthrene by heating.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 212](#)
- [Org. Syn. Coll. Vol. 3, 701](#)

References and Notes

1. Work done under contract with the Office of Scientific Research and Development.
2. Bachmann, *J. Am. Chem. Soc.*, **57**, 557 (1935).
3. Henstock, *J. Chem. Soc.*, **123**, 3097 (1923).
4. Bachmann, *J. Am. Chem. Soc.*, **56**, 1365 (1934); Hayduck, *Ann.*, **167**, 181 (1873); Anschutz, *Ber.*, **11**, 1217 (1878); Austin, *J. Am. Chem. Soc.*, **93**, 1763 (1908); Sandqvist, *Ann.*, **398**, 126 (1913); Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935); Mosettig and May, *J. Org. Chem.*, **11**, 15 (1946); Goldberg, Ordas, and Carsh, *J. Am. Chem. Soc.*, **69**, 260 (1947).

Appendix

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

[ethanol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[acetic acid](#) (64-19-7)

[hydrogen bromide](#) (10035-10-6)

[sodium carbonate](#) (497-19-8)

[bromine](#) (7726-95-6)

[carbon tetrachloride](#) (56-23-5)

sodium bisulfite (7631-90-5)

chromic anhydride

phenanthrene (85-01-8)

9-Bromophenanthrene,
Phenanthrene, 9-bromo- (573-17-1)

bromophenanthrene

phenanthrene dibromide