



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.

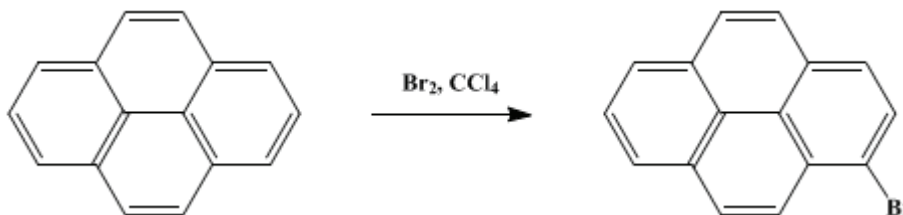
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.147 (1973); Vol. 48, p.30 (1968).

3-BROMOPYRENE

[Pyrene, 1-bromo-]



Submitted by W. H. Gumprecht¹

Checked by Melvin S. Newman and Stephen Havlicek.

1. Procedure

Caution! Many pyrenes are carcinogens. Contact of the skin with these materials should be avoided.

In a 500-ml., three-necked, round-bottomed flask fitted with a stirrer, a reflux condenser, and a dropping funnel are placed 8.08 g. (0.040 mole) of [pyrene](#) ([Note 1](#)) and 80 ml. of [carbon tetrachloride](#) ([Note 2](#)). A solution of 2.0 ml. of [bromine](#) (6.24 g., 0.039 mole) ([Note 3](#)) in 30 ml. of [carbon tetrachloride](#) is added dropwise over a period of 2–3 hours. The resulting orange solution is stirred overnight, washed with three 100-ml. portions of water, and dried over anhydrous [calcium chloride](#). The solvent is removed under reduced pressure, the pale yellow solid residue is dissolved in 10 ml. of [benzene](#), and the [benzene](#) solution is treated with a small amount of activated [carbon](#). The filtrate is diluted with 120 ml. of absolute [ethanol](#), and the solution is distilled until about 80–90 ml. of solvent remains and then cooled. The [bromopyrene](#) crystallizes as pale yellow flakes, m.p. 93–95°. Additional material of similar melting point is obtained from the mother liquor on concentration. The total yield is 8.5–9.5 g. (78–86%) ([Note 4](#)). On recrystallization from [benzene-alcohol](#) a colorless product, m.p. 94.5–95.5°, is obtained with little loss.

2. Notes

1. [Pyrene](#), m.p. 151–153°, obtained from Chemicals Division, Union Carbide Chemicals Corp., was used by the submitter. A commercial [pyrene](#) obtained from Germany was used by the checkers.
2. A C.P. solvent was used.
3. Reagent grade material was used. Excess [bromine](#) is to be avoided, as [dibromopyrene](#) can be formed.²
4. The submitter has run this preparation on 80 g. of [pyrene](#) with no change in yield.

3. Discussion

This procedure is described by Lock;² a modification using a small amount of [phenol](#) has been published.³ The patent literature discloses the use of a tertiary amine, such as [pyridine](#), and its combination with other solvents for the monobromination of [pyrene](#) with elemental [bromine](#).⁴ Brominating agents, such as [N-bromosuccinimide](#)⁵ and [N-bromohydantoin](#)s,⁶ have also been used.

4. Merits of the Preparation

[3-Bromopyrene](#) is a precursor of [3-hydroxypyrene](#).⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 632](#)

References and Notes

1. Contribution No. 334 from the Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19899.
 2. G. Lock, *Ber.*, **70**, 926 (1937).
 3. H. Hock and F. Ernst, *Ber.*, **92**, 2732 (1959).
 4. A. Wolfram and W. Schnurr, U.S. Patent 2,094,227 (1937) [*C.A.*, **31**, 8550 (1937)].
 5. Ng. Ph. Buu-Hoi and J. Lecocq, *Compt. Rend.*, **226**, 87 (1948).
 6. J. F. Salellas and O. O. Orazi, *Anales Asoc. Quim. Arg.*, **39**, 175 (1951) [*C.A.*, **47**, 2708 (1953)]; R. A. Corral, O. O. Orazi, and J. D. Bonafede, *Anales Asoc. Quim. Arg.*, **45**, 151 (1957) [*C.A.*, **53**, 342 (1959)].
 7. W. H. Gumprecht, *this volume*, p. 632.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

calcium chloride (10043-52-4)

Benzene (71-43-2)

phenol,
benzene-alcohol (108-95-2)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

carbon (7782-42-5)

pyridine (110-86-1)

pyrene (129-00-0)

N-bromosuccinimide (128-08-5)

3-Bromopyrene,
Pyrene, 1-bromo-,
bromopyrene (1714-29-0)

dibromopyrene

3-Hydroxypyrene (5315-79-7)