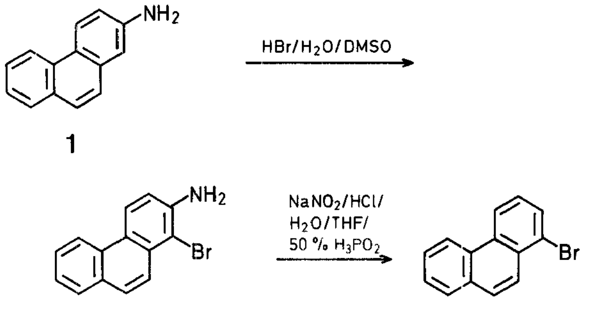
A Convenient Preparation of 1-Bromophenanthrene

Hsi-Lung Pan and T. Lloyd Fletcher

Pacific Northwest Research Foundation (The Fred Hutchinson Cancer Research Center), 1102 Columbia Street, Seattle, Washington 98104 U.S.A.

Conventional bromination of phenanthrene with bromine gives 9-bromophenanthrene or a mixture of dibromo derivatives, without formation of the 1-bromo isomer[1]. We now find that the latter (**3**), made previously by Bachman and Boatner[2] (involving a multistep synthesis of the precursor, 1-aminophenanthrene[3]) can be conveniently prepared from 2-amino-1-bromophenanthrene (**2**) which, in turn, is easily obtained in almost quantitative yield by brominating 2-aminophenanthrene (**1**) with 48% aqueous hydrobromic acid in dimethyl sulfoxide[4]. This greater accessibility of the 1-bromo compound thus makes possible (via a Grignard reaction, or a lithio derivative, etc.) the synthesis of otherwise difficultly obtainable, or unknown, 1-substituted phenanthrenes.



2-Amino-1-bromophenanthrene (2):

2-Aminophenanthrene (**1**; 2 g, 0.01 mol) prepared from 2-acetylphenanthrene (Aldrich) through a Schmidt rearrangement of the oxime and subsequent hydrolysis of the 2-acetamido derivative[3], was dissolved in dimethyl sulfoxide (15 ml). To the stirred solution 48% aqueous hydrobromic acid (0.01 mol) was added at 25°, drop by drop from a capillary dropper, over a period of 3.5 hr. After all the hydrobromic acid had been added the mixture was continuously stirred at 25° for 20 hr, heated under reflux at 95–100° (internal temperature) for 1 hr, and then allowed to cool to room temperature. The reaction solution was stirred into water, basified with dilute ammonium hydroxide, and the product collected by filtration; yield: 2.8 g (100%); m.p. 153–155°. Recrystallization from ethanol/water gave an analytical sample as colorless leaflets; m.p. 155.5–156.6°.

$C_{14}H_{10}BrN$	calc.	C 61.79	H 3.70	Br 29.36	N 5.15
(272.2)	found	61.67	3.87	29.38	5.17

I.R. (KBr): Strong bands at ν_{max} = 1620 (N—H), 807 (two adjacent H), 738 cm^{-1} (four adjacent H); other prominent bands at ν_{max} = 1462 (s), 1380 (m), 1198 (m), 1096 (m), 770 cm^{-1} (m).

The *N*-acetyl derivative, *2-acetamido-1-bromophenanthrene*, was obtained by acetylation of **2** with acetic acid/acetic anhydride at reflux temperature; yield: 90%; m.p. 241–242°.

$C_{16}H_{12}BrNO$	calc.	C 61.17	H 3.85	N 4.46
(314.2)	found	61.01	3.90	4.47

I.R. (KBr): Strong bands at ν_{max} = 3280, 1660 (amide), 810 (two adjacent H), 742 cm^{-1} (four adjacent H); other prominent bands at ν_{max} = 1610 (s), 1520 (s), 1480 (s), 1365 (s), 1302 (m), 1280 cm^{-1} (m).

1-Bromophenanthrene (3):

2-Amino-1-bromophenanthrene (**2**; 0.8 g, 3 mmol) was mixed with tetrahydrofuran (5 ml), conc. hydrochloric acid (30 ml), and water (10 ml). The suspension was stirred at 5–10° (internal temperature) while a solution of sodium nitrite (0.3 g, 4.5 mmol) in water (1.5 ml) was added dropwise in 5 min. After 30 min of stirring at 0–5°, the diazotization mixture was mixed with 50% hypophosphorous acid (15 ml). The mixture was stirred at 0° for another 30 min, then at ambient temperature for 17 hr, and diluted with water. The product (0.7 g) was collected on a filter and chromatographed on an alumina column, using benzene as eluent, and then recrystallized from methanol; yield: 0.5 g (66%); m.p. 109.5–110.5° (Ref.[2], m.p. 109.5–110°).

I.R. (KBr): Strong bands at ν_{max} = 817 (two adjacent H), 798 (three adjacent H), 740 cm^{-1} (four adjacent H); other prominent bands at ν_{max} = 1588 (m), 1452 (m), 1292 (m), 1202 (m), 1038 (m), 765 cm^{-1} (m).

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[1] See, e.g., H. Henstock, *J. Chem. Soc.* **1923**, 3097.
Further example: C.A. Dornfeld, J.E. Callen, G.H. Coleman, *Org. Synth.*, Coll. Vol. III, 134 (1955).

[2] W.E. Bachman, C.H. Boatner, *J. Amer. Chem. Soc.* **58**, 2194 (1936).

[3] W.E. Bachman, C.H. Boatner, *J. Amer. Chem. Soc.* **58**, 2097 (1936).

[4] T.L. Fletcher, H.-L. Pan, *J. Chem. Soc.* **1965**, 4588.