



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.

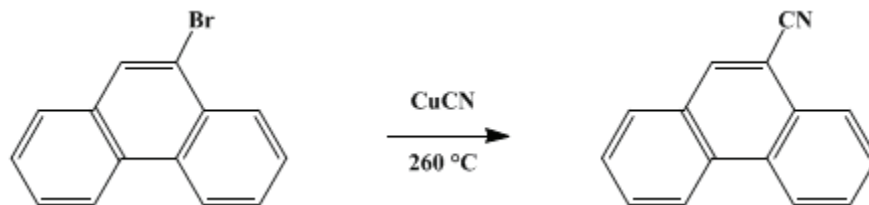
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 3, p.212 (1955); Vol. 28, p.34 (1948).*

## 9-CYANOPHENANTHRENE

### [9-Phenanthrenecarbonitrile]



Submitted by Joseph E. Callen, Clinton A. Dornfeld, and George H. Coleman<sup>1</sup>.  
Checked by Robert E. Carnahan and Homer Adkins.

### 1. Procedure

In a 2-l. Claisen flask (Note 1) are mixed 1 kg. (3.90 moles) of 9-bromophenanthrene (p. 134) (Note 2) and 400 g. (4.46 moles) of cuprous cyanide. A small motor-driven spiral stirrer is inserted, and the flask is heated (Note 3) at 260° for 6 hours (Note 4). The flask is then provided with a fine capillary inlet tube, a thermometer, and a 2-l. distilling flask attached to the side arm of the Claisen flask as receiver. The 9-cyanophenanthrene is distilled at 190–195°/2 mm. The yield of crude product is 740 g. (93%), m.p. 94–98°. One recrystallization from about 2 l. of dry ethanol yields 690 g. (87%) of material melting at 105–107° (Note 5), (Note 6), and (Note 7).

### 2. Notes

1. It is necessary to sacrifice the flask after the distillation, since the inorganic residue cannot be removed easily.
2. The 9-bromophenanthrene need not be recrystallized if it has been purified by distillation.
3. The heating may be readily controlled by the use of an electric heating mantle and variable transformer.
4. Increasing the heating period beyond 6 hours has no effect on the yield.
5. The melting point can be raised to 110° by further recrystallization from ethanol. The unrecrystallized product is probably pure enough for most purposes.
6. The checkers operated on one-tenth the scale and duplicated the percentage yields obtained on the larger scale. Material melting at 109–110° was obtained in a 75–77% yield.
7. It has been reported (W. R. Vaughan, private communication) that this reaction is highly exothermic, and that the flask contents may erupt when the mixture is heated to the prescribed temperature. Better control of the reaction may result if the cuprous cyanide is added in portions after the reaction has been initiated at 260–280° with about one-third or less of the total amount of cuprous cyanide.

### 3. Discussion

The procedure described above is an adaptation of methods of Mosettig and van de Kamp<sup>2</sup> and of Bachmann and Boatner.<sup>3</sup> 9-Cyanophenanthrene has also been prepared from 9-phenanthrenesulfonic acid<sup>4</sup> and from phenanthrene-9-aldoxime.<sup>5</sup>

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 26*

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### References and Notes

1. Work done under contract with the Office of Scientific Research and Development.
  2. Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **54**, 3355 (1932).
  3. Bachmann and Boatner, *J. Am. Chem. Soc.*, **58**, 2098 (1936); Goldberg, Ordas, and Carsh, *J. Am. Chem. Soc.*, **69**, 260 (1947).
  4. Werner and Kunz, *Ann.*, **321**, 327 (1902).
  5. Shoppee, *J. Chem. Soc.*, **1933**, 40.
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

ethanol (64-17-5)

Cuprous Cyanide (544-92-3)

9-Cyanophenanthrene,  
9-Phenanthrenecarbonitrile (2510-55-6)

9-Bromophenanthrene (573-17-1)

9-phenanthrenesulfonic acid

phenanthrene-9-aldoxime