



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.

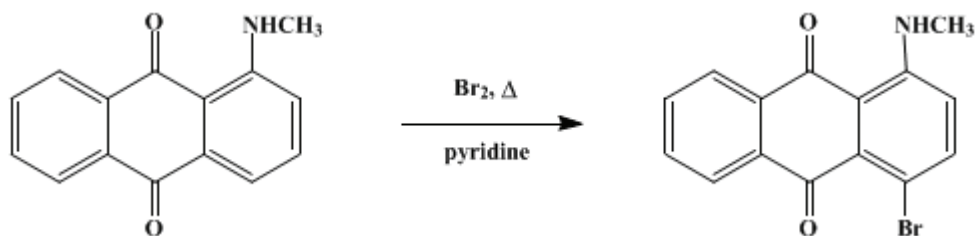
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.575 (1955); Vol. 29, p.68 (1949).

1-METHYLAMINO-4-BROMOANTHRAQUINONE

[Anthraquinone, 1-methylamino-4-bromo-]



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1. Procedure

In a 2-l. three-necked flask having ground-glass joints and equipped with a mechanical stirrer, a condenser (Note 1), and a dropping funnel are placed 119 g. (0.5 mole) of 1-methylaminoanthraquinone (p. 573) and 600 ml. of pyridine (Note 2) and (Note 3). The stirrer is started, and 90 g. (29 ml., 0.56 mole) of bromine is added over a period of 9–10 minutes. The flask and contents are now heated on the steam bath for 6 hours with continuous stirring. At the end of this period the hot mixture is transferred from the flask to a beaker and allowed to cool. The solid that separates (Note 4) is collected on a Büchner funnel and is washed thoroughly with hot water to remove a considerable portion of pyridine hydrobromide which is precipitated along with the desired product. The resulting deep red 1-methylamino-4-bromoanthraquinone, after thorough drying, weighs 111–117 g. (70–74%). It melts at 193–195° and is pure enough for most purposes (Note 5).

2. Notes

1. An air condenser of any type is sufficient.
2. A good grade of pyridine is essential. Very poor results are obtained with the practical or technical grades.
3. Larger volumes of pyridine have been used, but the yield drops progressively with increasing amounts.
4. Some of the solid separates during the heating on the steam bath.
5. It may be recrystallized, if desired, from pyridine, by the use of 3.5 ml. per g.; the melting point is raised to 195–196°.

3. Discussion

4-Bromo-1-methylaminoanthraquinone has been prepared from 4-bromo-1-nitroanthraquinone and methylamine at 60°,¹ and from 1-methylaminoanthraquinone in pyridine solution by treatment with two moles of bromine.² This procedure is based on the latter method.

References and Notes

1. Ger. pat. 144,634 [*Frdl.*, 7, 201 (1902–1904)].
 2. Ger. pat. 164,791 [*Frdl.*, 8, 280 (1905–1907)].
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Appendix

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

bromine (7726-95-6)

pyridine hydrobromide (18820-82-1)

pyridine (110-86-1)

methylamine (74-89-5)

1-METHYLAMINOANTHRAQUINONE (82-38-2)

1-Methylamino-4-bromoanthraquinone,
Anthraquinone, 1-methylamino-4-bromo-,
4-Bromo-1-methylaminoanthraquinone (128-93-8)

4-bromo-1-nitroanthraquinone