



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.

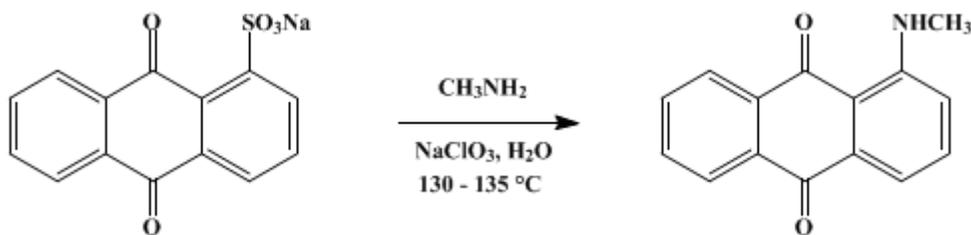
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.573 (1955); Vol. 29, p.66 (1949).

1-METHYLAMINOANTHRAQUINONE

[Anthraquinone, 1-methylamino-]



Submitted by C. V. Wilson, J. B. Dickey, and C. F. H. Allen.

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1. Procedure

A 1-gal. autoclave (p. 80) (Note 1) is charged with 399 g. (1.29 moles) of technical sodium anthraquinone- α -sulfonate (Note 2), 45 g. (0.43 mole) of sodium chlorate, 780 g. (6.25 moles) of a 25% aqueous solution of methylamine, and 1.2 l. of water. The mixture is heated, with stirring, for 12 hours at 130–135° (Note 3). The heat is then shut off, but stirring is continued so that the product separates in an easily removable form. When cold, the autoclave is opened and the contents are removed; the material adhering to the walls is removed by water. The solid is filtered on a 13-cm. Büchner funnel. The red product is washed with two 500-ml. portions of hot water (70°) and dried in the air. The yield of 1-methylaminoanthraquinone, melting at 166–171° (Note 4), is 180–199 g. (59–65%) (Note 5) and (Note 6).

2. Notes

1. A shaking autoclave employed for high-pressure hydrogenations may be used equally well, but the quantities taken must be reduced to 155 g. (0.5 mole) of sodium anthraquinone- α -sulfonate, 17.5 g. of sodium chlorate, 300 g. of a 25% aqueous methylamine solution, and 600 ml. of water. The checkers used a 2-gal. stirred autoclave (stainless steel).
2. A corresponding quantity of the potassium salt¹ can be utilized.
3. According to the checkers the heating time may be decreased to 8 hours if desirable.
4. The melting point varies slightly with the method of heating; if the bath is preheated to 160° before the sample is inserted, the melting point is 168–169.5°. When taken in the ordinary way, the melting point is 166–171°. This product is sufficiently pure for most purposes. One recrystallization from toluene raises the melting point 1°.
5. The yield depends upon the purity of the sodium anthraquinone- α -sulfonate. Apparent yields of as high as 87% have been obtained. The checkers employed technical-grade material, which apparently resulted in an appreciable decrease in the yields of 76–80% reported by the submitters.
6. α -Chloroanthraquinone² can be used as a starting material. In this case, 433 g. (1.79 moles) is taken, together with 1.5 l. of pyridine, 600 ml. of 25% aqueous methylamine, and 2.5 g. of a copper salt. The product is washed with dilute (2%) hydrochloric acid. The yield is 380–400 g. (90–95%).

3. Discussion

1-Methylaminoanthraquinone has been prepared from 1-chloro-, 1-bromo-, and 1-nitroanthraquinone by treatment with alcoholic methylamine under pressure,³ from 1-methoxy- and 1-phenoxyanthraquinone with methylamine in pyridine solution at 150°;⁴ from potassium anthraquinone-1-sulfonate with aqueous methylamine at 150–160°;^{5,6} from 1-aminoanthraquinone by treatment with formaldehyde,⁷ or methanol⁸ in sulfuric acid or oleum; and by hydrolysis of *p*-toluenesulfonylmethylaminoanthraquinone with sulfuric acid.⁹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 575](#)

References and Notes

1. [Org. Syntheses Coll. Vol. 2, 539 \(1943\)](#).
2. [Org. Syntheses Coll. Vol. 2, 128 \(1943\)](#).
3. Ger. pat. 144,634 [[Frdl.](#), **7**, 201 (1902–1904)].
4. Ger. pat. 165,728 [[Frdl.](#), **8**, 289 (1905–1907)].
5. Ger. pat. 175,024 [[Frdl.](#), **8**, 283 (1905–1907)].
6. Ger. pat. 256,515 [[Frdl.](#), **11**, 551 (1912–1914)].
7. Ger. pat. 156,056 [[Frdl.](#), **8**, 288 (1905–1907)].
8. Ger. pat. 288,825 [[Frdl.](#), **12**, 414 (1914–1916)].
9. Ullmann and Fodor, *Ann.*, **380**, 320 (1911).

Appendix

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

copper salt

1-chloro-, 1-bromo-, and 1-nitroanthraquinone

1-methoxy- and 1-phenoxyanthraquinone

sulfuric acid or oleum

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

[hydrochloric acid \(7647-01-0\)](#)

[methanol \(67-56-1\)](#)

[formaldehyde \(50-00-0\)](#)

[pyridine \(110-86-1\)](#)

[toluene \(108-88-3\)](#)

[sodium chlorate \(7775-09-9\)](#)

[methylamine \(74-89-5\)](#)

[\$\alpha\$ -Chloroanthraquinone \(82-44-0\)](#)

[potassium anthraquinone-1-sulfonate \(30845-78-4\)](#)

[1-aminoanthraquinone \(82-45-1\)](#)

1-METHYLAMINOANTHRAQUINONE,
Anthraquinone, 1-methylamino- (82-38-2)

sodium anthraquinone- α -sulfonate (128-56-3)

p-toluenesulfonylmethylaminoanthraquinone