



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.

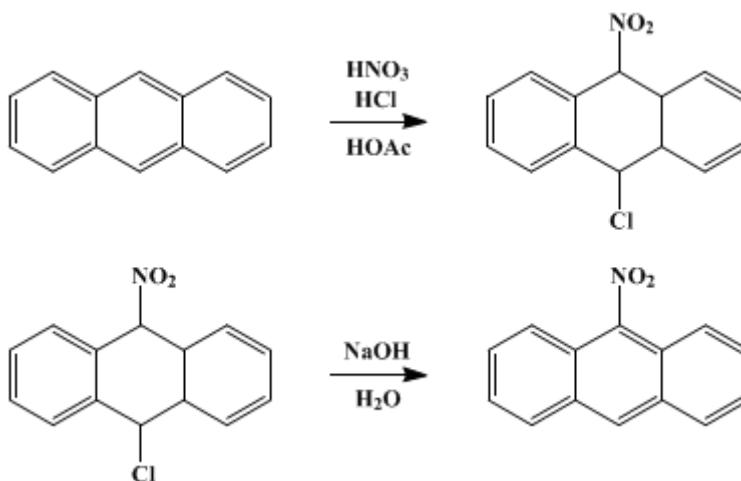
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.711 (1963); Vol. 31, p.77 (1951).

9-NITROANTHRACENE

[Anthracene, 9-nitro-]



Submitted by Charles E. Braun, Clinton D. Cook, Charles Merritt, Jr., and Joseph E. Rousseau¹.
Checked by William S. Johnson, George N. Sausen, and Paul R. Shafer.

1. Procedure

Twenty grams (0.112 mole) of finely powdered [anthracene](#) ([Note 1](#)) is suspended in 80 ml. of glacial [acetic acid](#) ([Note 2](#)) in a 500-ml. three-necked round-bottomed flask fitted with a 150-ml. dropping funnel, a thermometer, and an efficient motor-driven stirrer. The flask is immersed in a water bath at 20–25°, and 8 ml. (0.126 mole) of concentrated [nitric acid](#) (70% by weight, sp. gr. 1.42), essentially free of oxides of nitrogen, is added slowly from the dropping funnel with vigorous stirring. The rate of addition is controlled so that the reaction temperature does not exceed 30°. About 15–20 minutes is required for this step.

After all the [nitric acid](#) has been added, the mixture is stirred until a clear solution is obtained (about 30 minutes), and stirring is then continued for an additional 30 minutes. The solution is filtered to remove any [anthracene](#), and a mixture of 50 ml. (0.60 mole) of concentrated [hydrochloric acid](#) (37% by weight, sp. gr. 1.19) and 50 ml. of glacial [acetic acid](#) is added slowly to the filtrate with vigorous stirring. The pale-yellow precipitate of [9-nitro-10-chloro-9,10-dihydroanthracene](#) which forms is separated by suction filtration on a sintered-glass funnel and is washed with two 25-ml. portions of glacial [acetic acid](#) and then with water until the washings are neutral. The product is removed from the funnel and triturated thoroughly with 60 ml. of warm (60–70°) 10% [sodium hydroxide](#) solution ([Note 3](#)). The crude orange [nitroanthracene](#) is separated from the warm slurry by suction filtration and is treated with four 40-ml. portions of 10% [sodium hydroxide](#) solution ([Note 3](#)). The product is finally washed thoroughly with warm water until the washings are neutral to litmus. This treatment requires about 1.5–2 l. of water. The crude [9-nitroanthracene](#) is air-dried and recrystallized from glacial [acetic acid](#) ([Note 2](#)) and ([Note 4](#)). The yield of bright orange-yellow needles is 15–17 g. (60–68%), m.p. 145–146°.

2. Notes

1. [Anthracene](#) of good quality is required. The Eastman Kodak Company product, m.p. 215–217°, is satisfactory, or practical grade [anthracene](#) may be purified by codistillation with [ethylene glycol](#).²
2. The checkers employed E. I. du Pont de Nemours and Company, Inc., C.P. [acetic acid](#), which was further purified by distillation from [potassium permanganate](#).
3. The checkers found it desirable to carry out the trituration by grinding the mixture in a mortar,

because the nitrochloride has a tendency to form small, hard granules which otherwise may not come in contact with the alkali. The later treatments with alkali may be carried out satisfactorily in a beaker, or directly on the funnel, if thorough mixing is obtained. It is desirable to remove as much of the mother liquor as possible by suction from each of the alkali treatments.

4. For recrystallization, 10 ml. of glacial [acetic acid](#) is used for each gram of dried product. It is important that the dissolution be carried out rapidly; otherwise some decomposition may occur, producing [anthraquinone](#) as a contaminant. A satisfactory technique is to add the crude, dried, and crushed product rapidly in small portions to the total amount of boiling [acetic acid](#). The solution should then be filtered through a steam-heated funnel.

3. Discussion

The procedure described is a modification of that of Dimroth.³ [9-Nitroanthracene](#) has also been prepared by nitration of [anthracene](#) with [copper nitrate](#) in glacial [acetic acid](#) and with diacetylorthonitric acid.⁴ Other methods include direct nitration in [acetic acid](#) solution with [nitric acid](#) and [acetic anhydride](#),⁵ or by nitryl fluoride.⁶

References and Notes

1. University of Vermont, Burlington, Vermont.
2. Fieser, *Experiments in Organic Chemistry*, 2nd ed., p. 345, footnote 13, D. C. Heath and Company, Boston, Massachusetts, 1941.
3. Dimroth, *Ber.*, **34**, 221 (1901).
4. Braun, Cook, and Rousseau, unpublished work.
5. Meisenheimer and Connerade, *Ann.*, **330**, 133 (1904).
6. Hetherington and Robinson, *J. Chem. Soc.*, **1954**, 3512.

Appendix

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

oxides of nitrogen

diacetylorthonitric acid

nitryl fluoride

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

[acetic acid](#) (64-19-7)

[acetic anhydride](#) (108-24-7)

[sodium hydroxide](#) (1310-73-2)

[nitric acid](#) (7697-37-2)

[potassium permanganate](#) (7722-64-7)

[Anthraquinone](#) (84-65-1)

ethylene glycol (107-21-1)

anthracene (120-12-7)

copper nitrate (3251-23-8)

9-Nitroanthracene,
Anthracene, 9-nitro- (602-60-8)

9-nitro-10-chloro-9,10-dihydroanthracene

nitroanthracene