Organic Syntheses

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.

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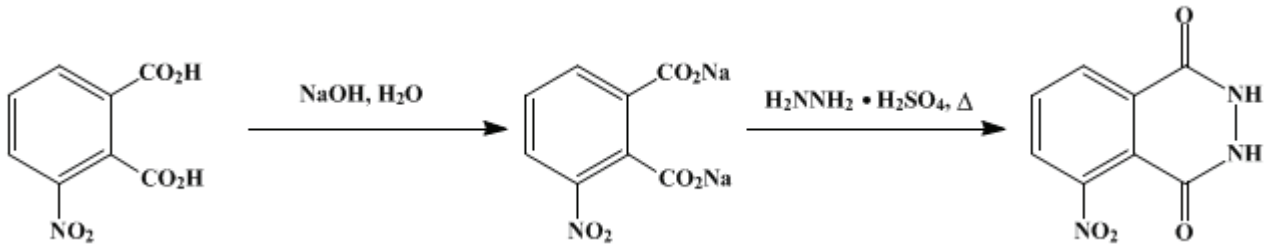
Organic Syntheses, Coll. Vol. 3, p.656 (1955); Vol. 29, p.78 (1949).

5-NITRO-2,3-DIHYDRO-1,4-PHTHALAZINEDIONE

[1,4-Phthalazinedione, 5-nitro-2,3-dihydro-]



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1. Procedure

In a 16-cm. evaporating dish are placed 42.2 g. (0.2 mole) of 3-nitrophthalic acid,[1] 50 ml. of water, and a few drops of phenolphthalein indicator solution. The mixture is made faintly alkaline to phenolphthalein with about 66 ml. (0.4 mole) of 6 *N* sodium hydroxide solution (Note 1), the last portions of which are added slowly with good stirring so that the end point may be observed. The color of the phenolphthalein is discharged by the addition of 0.2–0.3 g. of the 3-nitrophthalic acid, and 26.0 g. (0.2 mole) of hydrazine sulfate[2] is added. The solution is evaporated to dryness over a sand bath, with stirring at the latter part of the evaporation (Note 2), and the residual solid is cooled, ground in a mortar to a fine powder, and placed in a 200-ml. conical flask with 25 ml. of tetralin (Note 3). The mixture is heated at 160–170° for 3 hours and allowed to cool. After the addition of 50 ml. of benzene the solid is collected on a Büchner funnel and pressed down well, and most of the benzene is removed by suction. The solid is then washed with two 25-ml. portions of ether and allowed to stand in the air until the odor of ether is no longer detectable. The resulting material, weight 62–68 g., is an equimolar mixture of sodium sulfate and 5-nitro-2,3-dihydro-1,4-phthalazinedione, and it may be used directly for preparing 5-amino-2,3-dihydro-1,4-phthalazinedione (luminol, p. 69).

For purification, the crude material is suspended in 600–700 ml. of boiling water, and solid sodium carbonate is added in portions until the nitro compound has dissolved. Decolorizing carbon is added cautiously, and the suspension is boiled for a few minutes and filtered. The clear red-brown filtrate is acidified with concentrated hydrochloric acid, and the 5-nitro-2,3-dihydro-1,4-phthalazinedione is precipitated as a cream-colored flocculent solid. The solution is allowed to cool to room temperature, and the solid is separated by filtration and dried. The product thus obtained weighs 31–32 g. (75–78%) and has a melting point of 315–316° (dec.) when determined with the Kullman copper block (Note 4).

2. Notes

1. The strength of the sodium hydroxide solution is not critical; the equivalent amount of a solution of a different concentration may be used.
2. It is wise to cover the hand with a cloth or a glove while stirring, for the hot mixture may spatter if the heating is too rapid. The evaporation may be finished by transferring the evaporating dish to an oven shortly after the solid begins to separate. It is necessary to continue the evaporation until the solid is completely dry.
3. In an optional procedure the dry powder is heated in an oven at 160–170° for 3 hours.
4. No satisfactory solvent has been found for the recrystallization of 5-nitro-2,3-dihydro-1,4-phthalazinedione, but this precipitation gives a satisfactory product, free of sodium sulfate. The melting points given in the literature range from 297° to 320°.

3. Discussion

5-Nitro-2,3-dihydro-1,4-phthalazinedione has been prepared by heating 3-nitrophthalic acid with a large excess of hydrazine hydrate,[3] by heating 3-nitrophthalic acid with hydrazine sulfate[4] and sodium acetate, and by heating the nitro acid with hydrazine hydrate in ethanol at 150°.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 69

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 408 (1941).
2. *Org. Syntheses* Coll. Vol. **1**, 309 (1941).
3. Bogert and Boroschek, *J. Am. Chem. Soc.*, **23**, 740 (1901).
4. Huntress, Stanley, and Parker, *J. Am. Chem. Soc.*, **56**, 241 (1934).
5. Radulescu and Alexa, *Z. physik. Chem.*, **B8**, 393 (1930).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

3-Nitrophthalic acid (603-11-2)

decolorizing carbon (7782-42-5)

hydrazine hydrate (7803-57-8)

Hydrazine sulfate (10034-93-2)

phenolphthalein (77-09-8)

Tetralin (119-64-2)

5-Amino-2,3-dihydro-1,4-phthalazinedione (521-31-3)

5-Nitro-2,3-dihydro-1,4-phthalazinedione,
1,4-Phthalazinedione, 5-nitro-2,3-dihydro- (3682-15-3)