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.

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.

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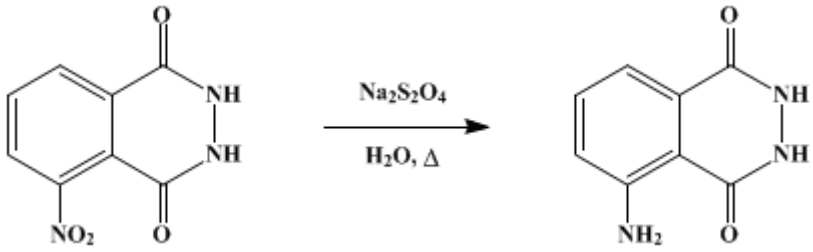
5-AMINO-2,3-DIHYDRO-1,4-PHTHALAZINEDIONE

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



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1. Procedure

In a 1-l. conical flask are placed 52 g. (about 0.15 mole) of the equimolecular mixture of 5-nitro-2,3-dihydro-1,4-phthalazinedione (p. 656) and sodium sulfate (Note 1), 200 ml. of water, and 75 ml. of 15 *N* ammonium hydroxide solution (sp. gr. 0.90). The flask is stoppered and shaken until all, or very nearly all, of the solid has dissolved, and 84 g. (0.4 mole) of sodium hydrosulfite dihydrate (Note 2) is added in three portions. The solution becomes hot, the temperature sometimes reaching the boiling point, and the dark orange-red color begins to fade. After the spontaneous reaction has subsided the solution is boiled gently for a few minutes and filtered to remove insoluble impurities. The filtrate is heated on a steam bath or over a small flame for 30 minutes. During this time the 5-amino-2,3-dihydro-1,4-phthalazinedione begins to separate as a light-yellow flocculent precipitate or as a crust adhering to the walls of the flask. The hot solution is made distinctly acid to litmus paper with glacial acetic acid and allowed to stand overnight. The yellow precipitate is separated by filtration, washed well with cold water, and dried in a hot-air oven at 110° or below. The dry material weighs 25–27 g. and melts with decomposition at 301–305° (Note 3).

This material is sufficiently pure for most purposes. The chief impurities are small amounts of inorganic salts and a trace of the unreduced nitro compound. If a purer product is desired the crude material (5 g. per 100 ml.) is dissolved in hot 3 *N* hydrochloric acid, decolorizing carbon is added, the solution is filtered promptly (Note 4), and the filtrate is made just faintly acid to Congo red paper with concentrated ammonium hydroxide. After the mixture has cooled to room temperature the pale yellow flocculent precipitate is separated by filtration, washed well with cold water, and dried in the oven at 100° or below. The recovery in the crystallization is 70–75% (Note 5), and the product melts at 329–332° (Note 4).

2. Notes

1. No advantage is gained by using the purified nitro compound.
2. The success of this reduction depends upon the quality of the sodium hydrosulfite. The reagent should be taken from a fresh bottle; material which has stood in the laboratory for a long time probably has undergone oxidation.
3. The submitters used a Kullmann copper block for the melting-point determinations. The melting point of the pure material has been reported in the literature at various values between 319° and 333°.
4. The 5-amino-2,3-dihydro-1,4-phthalazinedione should not be exposed to hot hydrochloric acid longer than necessary, since some hydrolysis appears to take place.
5. The percentage yield cannot be calculated with precision, since the exact quantity of nitro compound in the mixture taken for the reduction is unknown. The quantity of sodium hydrosulfite dihydrate employed is sufficient for the reduction of only 0.133 mole of nitro compound; the weight of the purified amino compound corresponds to about 80% of the theoretical yield calculated on the

assumption that the hydrosulfite is the limiting reagent.

3. Discussion

5-Amino-2,3-dihydro-1,4-phthalazinedione, also called luminol and 3-aminophthalhydrazide, has been prepared from 5-nitro-2,3-dihydro-1,4-phthalazinedione by reduction with ammonium sulfide[1] or stannous chloride[2] and by catalytic hydrogenation over palladium on charcoal in alkaline solution[3] and by the reaction of 3-aminophthalimide[2] with hydrazine hydrate.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 656

References and Notes

1. Huntress, Stanley, and Parker, *J. Am. Chem. Soc.*, **56**, 241 (1934).
2. Drew and Pearman, *J. Chem. Soc.*, **1937**, 30.
3. Wegler, *J. prakt. Chem.*, **148**, 135 (1937).

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

luminol

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

sodium sulfate (7757-82-6)

sodium hydrosulfite (7775-14-6)

stannous chloride

decolorizing carbon (7782-42-5)

palladium (7440-05-3)

ammonium hydroxide (1336-21-6)

hydrazine hydrate (7803-57-8)

ammonium sulfide

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

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

sodium hydrosulfite dihydrate

3-aminophthalimide (2518-24-3)