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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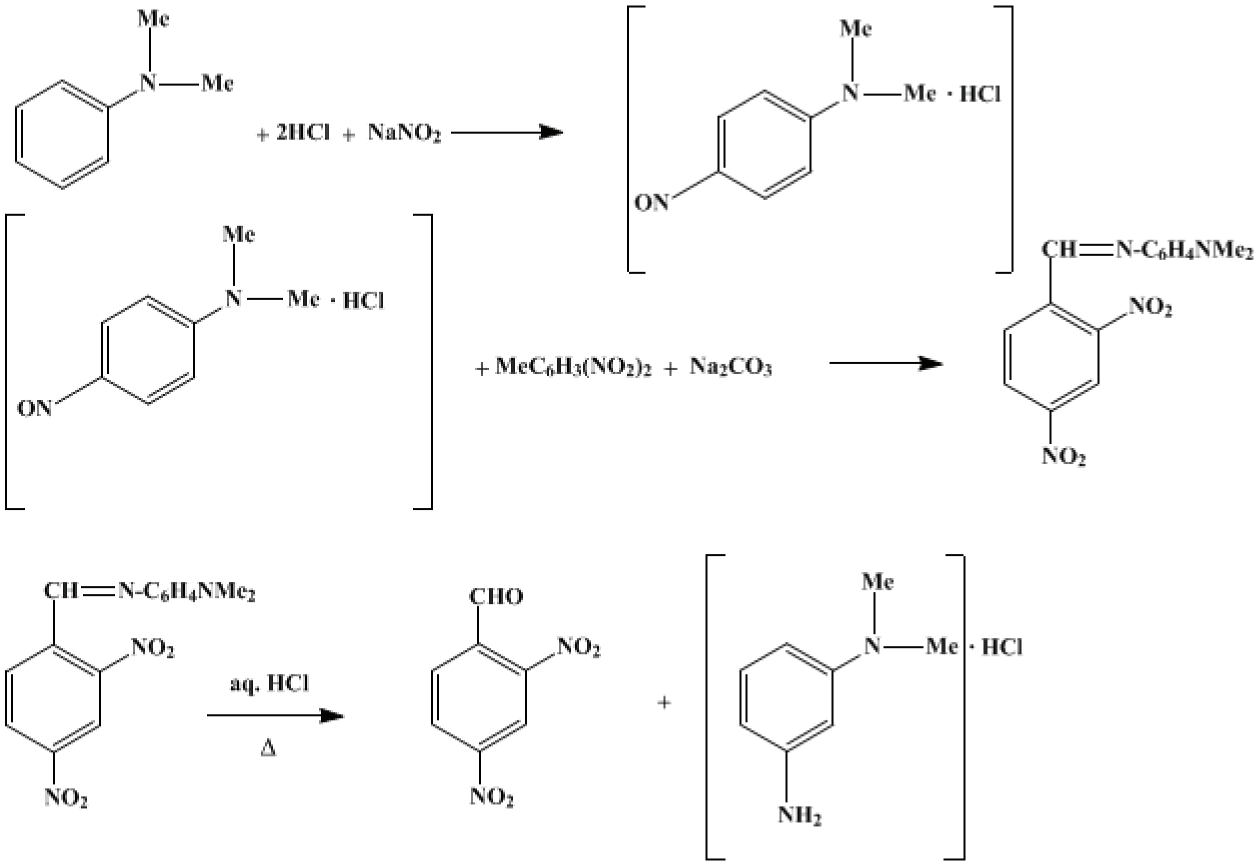
2,4-DINITROBENZALDEHYDE

[Benzaldehyde, 2,4-dinitro-]



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1. Procedure

A solution of 300 g. (2.5 moles) of technical dimethylaniline in 1050 cc. of concentrated hydrochloric acid is placed in a large jar or crock and finely divided ice is added until the temperature has fallen to 5°. The contents of the jar are then stirred mechanically, and a solution of 180 g. (2.6 moles) of sodium nitrite in 300 cc. of water is slowly added from a separating funnel, the stem of which dips beneath the surface of the liquid. The addition takes one hour, and the temperature is kept below 8° by the addition of ice if necessary. When all the nitrite has been added the mixture is allowed to stand one hour and then filtered. The solid *p*-nitrosodimethylaniline hydrochloride is washed with 400 cc. of 1:1 hydrochloric acid and then with 100 cc. of alcohol. After drying in air, it weighs 370–410 g. (80–89 per cent of the theoretical amount) (Note 1).

In a 3-l. flask a mixture of 330 g. (1.8 moles) of air-dried *p*-nitrosodimethylaniline hydrochloride (Note 2) with 100 g. of anhydrous sodium carbonate and 1.5 l. of 95 per cent alcohol is heated on the steam bath for thirty minutes and filtered to remove sodium chloride and unchanged carbonate. The filtrate is placed with 300 g. (1.6 moles) of 2,4-dinitrotoluene (m.p. 70°) in a 5-l. flask provided with a mechanical stirrer and a reflux condenser and heated on the steam bath with stirring for five hours. When the contents of the flask are cold, the condensation product is collected on a Büchner funnel and well drained by means of a suction pump and a piece of "rubber dam" fastened over the top of the funnel. The rubber is drawn down onto the solid by the suction, thus forcing the liquid out. The dark green solid is washed by transferring it to a large beaker, stirring it with 1 l. of 95 per cent alcohol on the steam bath for half an hour, cooling, and filtering again, using the rubber dam. The dinitrobenzylidene-*p*-aminodimethylaniline is placed while still damp in a large round-bottomed flask containing 500 cc. of a mixture of equal volumes of concentrated hydrochloric acid and water, and steam is blown in by a tube reaching to the lowest part of the vessel. Vigorous injection of steam is continued for fifteen minutes after the liquid has reached a temperature of 105° (Note 3).

When cold the aqueous layer is decanted (or filtered) from the solidified product, and the process of steam-agitation with acid is repeated, another 500 cc. of dilute acid being added (Note 4). Finally the solid is filtered, washed with water, and dried *in vacuo*. The crude dinitrobenzaldehyde so obtained weighs 170–210 g. and melts at 40–50°. It is purified by heating in two lots each with 8 l. of naphtha (b.p. 90–110°) in a large flask on the steam bath with mechanical stirring for three hours, decanting the solution (temperature of liquid 80°) and allowing the aldehyde to crystallize. The purified dinitrobenzaldehyde, air-dried, weighs 79–104 g. (24–32 per cent of the theoretical amount) and melts at 69–71° (Note 5). From the mother liquors impure material may be recovered by evaporation or by distillation in steam, from which by a similar process of crystallization a further 20 g. of aldehyde of m.p. 66° can be separated.

2. Notes

1. It is reported that *p*-nitrosodiethylaniline hydrochloride can be prepared by a similar procedure and that the free base can be obtained from the hydrochloride in the following way: The reaction mixture containing the *p*-nitrosodiethylaniline hydrochloride prepared from 50 g. of once-distilled diethylaniline is stirred and kept at 5° while 580 cc. of 2 *N* sodium carbonate solution is added dropwise. The addition requires about two hours, after which the color of the reaction mixture changes to dark green and a dark green solid separates. Stirring is continued for ten minutes, then the precipitate is allowed to settle for five minutes and is filtered with suction. The precipitate is washed with three 25-cc. portions of distilled water, added dropwise by means of a pipet, then with three 20-cc. portions of a 1:1 alcohol-ether mixture, also added dropwise. The *p*-nitrosodiethylaniline is dried in a desiccator over calcium chloride. The material weighs 57 g. (95 per cent of the theoretical amount). If a very pure sample is desired, the nitrosoamine should be crystallized from petroleum ether. (M. Q. Doja and A. Mokeet, private communication.)
2. Attempts to use technical nitrosodimethylaniline in place of the freshly prepared material were not successful.
3. It is essential that the temperature reach the maximum (about 105°) and be kept at this point for sufficient time during the hydrolysis.
4. The acid aqueous liquors contain *p*-aminodimethylaniline and might be utilized in the preparation of quinoneimine dyes.
5. 2,4-Dinitrobenzaldehyde is a useful reagent since it forms crystalline condensation products with amines and with substances having a reactive methylene or methyl group.[1]

3. Discussion

Dinitrobenzaldehyde was first prepared from dinitrotoluene.[1], [2], [3] It has also been prepared from 2,4-dinitrobenzylaniline by oxidation to the benzylidene compound and subsequent hydrolysis,[4], [5] and by oxidation of dinitrobenzyl alcohol.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 825

References and Notes

1. Bennett and Pratt, J. Chem. Soc. **1929**, 1465.
2. Sachs and Kempf, Ber. **35**, 1224 (1902); Sachs, Ger. pat. 121,745 [Frdl. **6**, 1047 (1900–02)].

3. Müller, Ber. **42**, 3695 (1909).
4. Sachs and Everding, ibid. **35**, 1237 (1902).
5. Cohn and Friedländer, ibid. **35**, 1266 (1902).

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

petroleum ether

naphtha

alcohol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sodium nitrite (7632-00-0)

dimethylaniline (121-69-7)

2,4-Dinitrobenzaldehyde,
Benzaldehyde, 2,4-dinitro- (528-75-6)

dinitrobenzaldehyde

diethylaniline (91-66-7)

nitrosodimethylaniline

2,4-dinitrobenzylaniline

dinitrobenzyl alcohol

2,4-dinitrotoluene,
dinitrotoluene (121-14-2)

quinoneimine

p-Nitrosodimethylaniline hydrochloride (42344-05-8)

dinitrobenzylidene-p-aminodimethylaniline p-nitrosodiethylaniline hydrochloride (58066-98-1)

p-Nitrosodiethylaniline (120-22-9)

p-aminodimethylaniline (99-98-9)