



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.

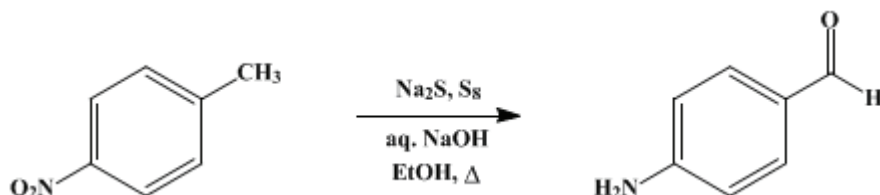
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***p*-AMINOBENZALDEHYDE**

[Benzaldehyde, *p*-amino-]



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1. Procedure

To 600 ml. of distilled water in a 1-l. beaker are added 30 g. (0.125 mole) of crystalline [sodium sulfide nonahydrate](#) (Note 1), 15 g. (0.47 g. atom) of flowers of [sulfur](#), and 27 g. (0.67 mole) of [sodium hydroxide](#) pellets. The mixture is heated on a steam bath for 15–20 minutes with occasional stirring and then poured into a 2-l. round-bottomed flask containing a hot solution of 50 g. (0.36 mole) of *p*-nitrotoluene (Note 2) in 300 ml. of 95% [ethanol](#). A reflux condenser is attached, and the mixture is heated under reflux for 3 hours. The resulting clear but deep red solution is rapidly steam-distilled until about 1.5–2 l. of condensate has been collected (Note 3). The distillate should be clear when the distillation is stopped. The residue in the 2-l. flask should have a volume of 500–600 ml.; if less, it should be diluted to this volume with boiling water. The solution is rapidly chilled in an ice bath with occasional vigorous shaking and stirring to induce crystallization. After 2 hours in the ice bath the golden yellow crystals of *p*-aminobenzaldehyde are collected on a Büchner funnel and washed with 500 ml. of ice water to remove [sodium hydroxide](#) (Note 4). The product is immediately placed in a vacuum desiccator over solid [potassium hydroxide](#) pellets for 24 hours. The yield of *p*-aminobenzaldehyde, m.p. 68–70°, amounts to 18–22 g. (40–50%). The product contains some impurities but is pure enough for most purposes (Note 5). It should be stored in a sealed bottle (Note 6).

2. Notes

1. Merck's reagent grade of [sodium sulfide nonahydrate](#) was used. Since [sodium sulfide](#) decomposes on contact with air, a freshly opened bottle should be employed. "Sodium Sulphydrate" (Hooker Electrochemical Company hydrated [sodium hydrosulfide](#)) is also satisfactory; the amount should be based upon the formula $\text{NaHS}\cdot 2\text{H}_2\text{O}$, and an equivalent amount of [sodium hydroxide](#) in excess of the 27 g. is required.

2. The *p*-nitrotoluene used was Eastman Kodak Company practical grade.

3. The steam distillation should be carried out as rapidly as possible. The distillate contains [ethanol](#), *p*-toluidine, and some unchanged *p*-nitrotoluene.

It has been reported² that a large amount of a dark oily tar may be present at this stage. Presumably it consists of Schiff's base polymers which have formed during the time necessary for reflux and steam distillation. The clear solution may be decanted from the oil, and the expected orange-yellow crystals of *p*-aminobenzaldehyde are obtained on cooling the solution.

The oily tar may be dissolved in boiling [acetic anhydride](#), and upon dilution of the reaction mixture with water and partial concentration, crude *p*-acetamidobenzaldehyde separates. The latter may be purified by dissolving it in hot [sodium bisulfite](#) solution and fractionally precipitating the aldehyde by the addition of [sodium hydroxide](#) solution. From 12.3 g. of intractable tars there were obtained a first fraction which consisted of a dark sludge which was discarded, a second fraction which weighed 5.2 g., m.p. 150°, and a third which weighed 1.9 g., m.p. 147°. The melting point of *p*-acetamidobenzaldehyde is recorded³ as 153°.

4. It is sometimes necessary to suspend the precipitate in about 200 ml. of ice water, stir it vigorously,

and filter again to remove all traces of alkali.

5. The chief impurities are the polymeric condensation products of *p*-aminobenzaldehyde with itself. No satisfactory method for recrystallization has been found. If the melting point is high and a pure product is desired, it is best to extract with boiling water until the filtrate is clear, and extract the monomer from the water with ether. This procedure gives recoveries of 25–30%.

Readily purified aldehyde derivatives may be prepared in good yields from the crude polymer mixture. The oxime melts at 124°, the azine at 245°, and the phenylhydrazone at 175°.⁴ If these derivatives are hydrolyzed, the same crude *p*-aminobenzaldehyde of broad melting range results.

6. Care must be taken to exclude all traces of acid fumes from *p*-aminobenzaldehyde, since they catalyze its self-condensation.

3. Discussion

p-Aminobenzaldehyde has been prepared by the action of sodium polysulfide upon *p*-nitrotoluene^{5,6,7,8} on which the method described is based. It can be prepared also from *p*-nitrobenzyl alcohol and sodium sulfide,⁶ by heating *p*-nitrobenzaldehyde with sodium bisulfite and decomposing the addition product with hydrochloric acid,⁹ by the reduction of *p*-nitrobenzaldoxime with ammonium sulfide^{3,10} and subsequent hydrolysis of the amino oxime, and by the decomposition of the benzenesulfonyl-hydrazide of *p*-aminobenzoic acid in the presence of powdered glass and sodium carbonate.¹¹

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 88

References and Notes

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3. Gabriel and Herzberg, *Ber.*, **16**, 2003 (1883).
4. Walther and Kausch, *J. prakt. Chem.*, [2] **56**, 97 (1897).
5. Geigy, Ger. pat. 86,874 (1895) [*Frld.*, **4**, 136 (1894–1897)]; Friedländer and Lenk, *Ber.*, **45**, 2087 (1912).
6. Beard and Hodgson, *J. Chem. Soc.*, **1944**, 4.
7. Mukherjee, Indian pat. 43,527 [*C. A.*, **46**, 7121 (1952)].
8. DeGarmo and McMullen (to Monsanto Chemical Co.) U. S. pat. 2,795,614 [*C. A.*, **51**, 16542 (1957)].
9. Meister Lucius and Brüning, Ger. pat. 106,590 (1898) [*Chem. Zentr.*, I **71**, 1084 (1900)].
10. Cohn and Springer, *Monatsh.*, **24**, 87 (1903).
11. Newman and Caflish, *J. Am. Chem. Soc.*, **80**, 862 (1958).

Appendix

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

sodium polysulfide

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ether (60-29-7)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

sulfur (7704-34-9)

sodium bisulfite (7631-90-5)

potassium hydroxide (1310-58-3)

sodium sulfide (1313-82-2)

ammonium sulfide

p-Nitrobenzaldehyde (555-16-8)

sodium hydrosulfide,
Sodium Sulfhydrate

sodium sulfide nonahydrate (1313-84-4)

p-toluidine (106-49-0)

benzenesulfonyl-hydrazide (80-17-1)

p-Nitrobenzyl alcohol (619-73-8)

p-aminobenzoic acid (150-13-0)

p-nitrotoluene (99-99-0)

p-Aminobenzaldehyde,
Benzaldehyde, p-amino- (17625-83-1)

p-nitrobenzaldoxime

p-acetamidobenzaldehyde (122-85-0)