



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](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.

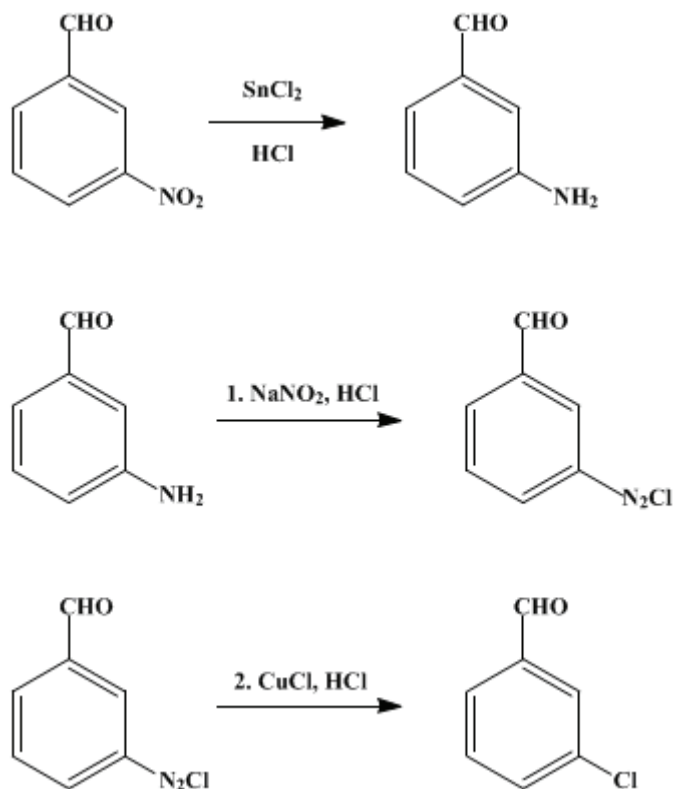
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 2, p.130 (1943); Vol. 13, p.28 (1933).*

## ***m*-CHLOROBENZALDEHYDE**

[Benzaldehyde, *m*-chloro-]



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### 1. Procedure

A solution of 450 g. (2 moles) of [stannous chloride](#) crystals ([Note 1](#)) in 600 cc. of concentrated [hydrochloric acid](#) is placed in a 3-l. beaker provided with an efficient mechanical stirrer and cooled in an ice bath. When the temperature of the solution has fallen to +5°, 100 g. (0.66 mole) of *m*-[nitrobenzaldehyde](#) ([Note 2](#)) is added in one portion. The temperature rises slowly at first, reaching 25–30° in about five minutes, then rises very rapidly to about 100°. Stirring must be vigorous or the reaction mixture may be forced out of the beaker ([Note 3](#)). During the reaction the [nitrobenzaldehyde](#) dissolves, and an almost clear, red solution is obtained. The solution is cooled in an ice-salt mixture until the temperature has fallen to about +2°. During the cooling, orange-red crystals separate and a pasty suspension results.

A 250-cc. separatory funnel is fixed so that its stem extends below the surface of the pasty suspension. A solution of 46 g. (0.67 mole) of [sodium nitrite](#) in 150 cc. of water is placed in the funnel and is slowly added to the well-stirred mixture until it shows a positive starch-iodide test for [nitrous acid](#). The temperature of the mixture is maintained between 0° and +5° ([Note 4](#)) throughout the addition of the nitrite solution, which requires about ninety minutes. Usually, all but 5–8 cc. of the nitrite solution must be added before a positive test for [nitrous acid](#) appears.

During the latter part of the diazotization of the [aminobenzaldehyde](#), a hot solution of [cuprous chloride](#) is prepared. In a 5-l. round-bottomed flask, 189 g. (0.75 mole) of powdered [copper sulfate](#) crystals and 161 g. of [sodium chloride](#) are dissolved in 600 cc. of hot water, and to this solution is added a solution of 41 g. (0.22 mole) of sodium metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) and 27 g. (0.67 mole) of [sodium](#)

hydroxide in 300 cc. of water. The final temperature of the resulting cuprous chloride solution should be about 75°.

The diazonium solution is added to the hot cuprous chloride solution while the latter is shaken by hand but is not cooled. After the solutions are thoroughly mixed, 840 cc. of concentrated hydrochloric acid is added and the mixture is allowed to stand overnight. The reaction mixture is steam-distilled to separate the *m*-chlorobenzaldehyde, which is collected practically completely in the first 1.5 l. of distillate. The *m*-chlorobenzaldehyde is removed from the aqueous distillate by extraction with two 150-cc. portions of ether, and the ethereal solution is dried with 10–15 g. of anhydrous calcium chloride. After being decanted from the drying agent, the ether is distilled, and the residual liquid is distilled under diminished pressure. The *m*-chlorobenzaldehyde boils at 84–86°/8 mm., 107–109°/26 mm. (Note 5). The yield is 70–74 g. (75–79 per cent of the theoretical amount) (Note 6).

## 2. Notes

1. A chemically pure grade of stannous chloride crystals ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was used. Lower yields were obtained when technical stannous chloride was used.
2. A practical grade of *m*-nitrobenzaldehyde was used; m.p. 52–55°.
3. During the vigorous reaction it is advisable to keep the cooling bath and the reaction mixture well stirred. Less satisfactory yields were obtained when the reaction was moderated by adding the nitrobenzaldehyde in several portions.
4. At temperatures below 0° the speed of diazotization is markedly decreased. Above +5° some decomposition of the diazonium salt takes place.
5. Since *m*-chlorobenzaldehyde is oxidized easily by atmospheric oxygen, it should be stored in a tightly corked or sealed container.
6. According to the submitters *m*-bromobenzaldehyde can be prepared by the same general procedure using, in place of cuprous chloride, a solution of cuprous bromide prepared from 189 g. of copper sulfate, 91 g. of sodium bromide, 41 g. of sodium metabisulfite, and 27 g. of sodium hydroxide. Instead of 840 cc. of concentrated hydrochloric acid, 200 cc. of 48 per cent hydrobromic acid is added after the diazonium solution has been mixed with the cuprous bromide. The *m*-bromobenzaldehyde boils at 93–98°/8 mm. The yield is 80 g. or 65 per cent of the theoretical amount. It is reported, however, that *m*-bromobenzaldehyde prepared in this way may contain as much as 20 per cent of *m*-chlorobenzaldehyde. This contamination can be avoided by using stannous bromide as the reducing agent.

A solution of stannous bromide is prepared by heating 119 g. (1 gram atom) of mossy tin with 705 g. (4 moles) of 46 per cent hydrobromic acid for two hours on a steam bath, with mechanical stirring. The solution is cooled to 40°, and 50 g. (0.33 mole) of *m*-nitrobenzaldehyde is added in one portion, with continued stirring. The temperature rises from the heat of reaction and finally reaches about 105°. After heating for one-half hour longer on a steam bath, the reaction mixture is cooled to 0° and the aminobenzaldehyde diazotized by the gradual addition of 23 g. (0.33 mole) of sodium nitrite in 75 cc. of water. The diazonium solution is poured into a hot suspension of cuprous bromide, 100 cc. of 46 per cent hydrobromic acid is added, with stirring, and the mixture is allowed to stand overnight. The mixture is steam-distilled and the *m*-bromobenzaldehyde isolated by ether extraction and vacuum distillation; b.p. 90–92°/4 mm. The yield is 41 g. (67 per cent of the theoretical amount). (F. T. Tyson, private communication.)

## 3. Discussion

*m*-Chlorobenzaldehyde has been prepared by the chlorination of benzaldehyde<sup>1</sup> and by the oxidation of *m*-chlorobenzyl alcohol<sup>2</sup> and of *m*-chlorotoluene.<sup>3</sup> It is most conveniently prepared from *m*-nitrobenzaldehyde through *m*-aminobenzaldehyde and the diazonium reaction.<sup>4</sup> The procedure given above is essentially that described in the patent literature.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 583
- Org. Syn. Coll. Vol. 3, 453

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## References and Notes

1. Müller, Ger. pat. 30,329; 33,064 [Frdl. **1**, 143, 146 (1877–87)].
  2. Mettler, Ber. **38**, 2812 (1905).
  3. Law and Perkin, J. Chem. Soc. **93**, 1636 (1908).
  4. Meister, Lucius, and Brüning, Ger. pat. 31,842 [Frdl. **1**, 144 (1877–87)]; Erdmann and Schwechten, Ann. **260**, 59 (1890); Eichengrün and Einhorn, *ibid.* **262**, 135 (1891).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sodium metabisulfite

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

HYDROBROMIC ACID (10035-10-6)

sodium bromide (7647-15-6)

oxygen (7782-44-7)

copper sulfate (7758-98-7)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

tin (7440-31-5)

stannous chloride

benzaldehyde (100-52-7)

cuprous bromide (7787-70-4)

cuprous chloride (7758-89-6)

nitrobenzaldehyde (552-89-6)

aminobenzaldehyde (529-23-7)

stannous bromide (10031-24-0)

m-Bromobenzaldehyde (3132-99-8)

m-Chlorobenzaldehyde,  
Benzaldehyde, m-chloro- (587-04-2)

m-Nitrobenzaldehyde (99-61-6)

m-chlorobenzyl alcohol (873-63-2)

m-chlorotoluene (108-41-8)

m-aminobenzaldehyde (1709-44-0)