



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.

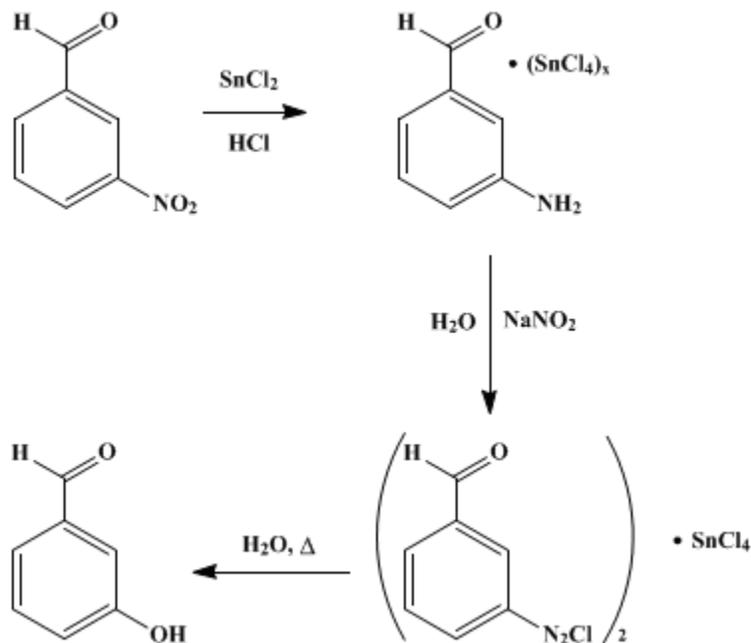
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.453 (1955); Vol. 25, p.55 (1945).

m-HYDROXYBENZALDEHYDE

[Benzaldehyde, *m*-hydroxy-]



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1. Procedure

A solution of 450 g. (2 moles) of powdered stannous chloride dihydrate (Note 1) in 600 ml. of concentrated hydrochloric acid in a 3-l. beaker provided with an efficient mechanical stirrer is cooled in an ice-salt bath. When the temperature of the solution has fallen to 5° , the ice bath is removed, and 100 g. (0.66 mole) of *m*-nitrobenzaldehyde (Note 2) is added in one portion. The temperature rises slowly at first, reaching $25\text{--}30^\circ$ in about 5 minutes. As it then rises rapidly to about 100° the ice-salt bath is again placed around the beaker. Stirring must be vigorous or the reaction mixture may be forced out of the beaker (Note 3). During the reaction the *m*-nitrobenzaldehyde dissolves, and an almost clear red solution is obtained. The solution is cooled with very slow stirring (Note 4) in an ice-salt mixture for 2.5 hours. The orange-red paste of the stannichloride of *m*-aminobenzaldehyde (Note 5) is filtered on a sintered-glass funnel (Note 6).

A suspension of the material in 600 ml. of concentrated hydrochloric acid is stirred mechanically in a 3-l. beaker which is set in an ice-salt bath. A solution of 46 g. of sodium nitrite in 150 ml. of water in a 250-ml. dropping funnel fixed with its stem below the surface of the suspension is added slowly while the temperature of the mixture is kept at $4\text{--}5^\circ$ (Note 7). After the addition is completed (in approximately 80 minutes), stirring in the ice-salt bath is continued for 1 hour to crystallize completely the stannichloride of the diazonium salt. The reddish brown salt is filtered on a sintered glass funnel (Note 6).

The damp salt is added cautiously in small portions to 1.7 l. of boiling water in a 4-l. beaker in the course of 40 minutes. During the reaction, the water lost by vaporization is replaced (Note 8). The solution is treated with 4 g. of Norit, boiled a few minutes, and filtered hot. The red filtrate is kept in an icebox for 12–16 hours; during this time scratching is employed occasionally to induce crystallization (Note 9). The yield of orange crystals melting at $99\text{--}101^\circ$ is 48–52 g. (59–64%). A solution of this product in about 1 l. of boiling benzene is treated with Norit, filtered, and concentrated to 300 ml. On

cooling, 41–45 g. (51–56%) of light-tan crystals melting at 101–102° is obtained (Note 10).

2. Notes

1. A chemically pure grade of [stannous chloride](#) ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) should be used. Lower yields are obtained with technical [stannous chloride](#).
2. A practical grade of [m-nitrobenzaldehyde](#) (m.p. 52–55°) was used by the submitter. The checkers used Eastman's [m-nitrobenzaldehyde](#) (m.p. 57–58°).
3. Less satisfactory yields are obtained when the reaction is moderated by the addition of the [m-nitrobenzaldehyde](#) in several portions.
4. Stirring must be very slow since gradual cooling is necessary in order to obtain particles large enough to permit fairly rapid filtration.
5. The exact formula of the [m-aminobenzaldehyde](#) stannichloride is not known.
6. As a substitute for the sintered-glass funnel, a large Büchner funnel provided with an asbestos fiber mat under the filter paper will serve. The asbestos mat can be washed and used repeatedly.
7. Best results are obtained by keeping the temperature during diazotization at 4–5°. Below 0° the speed of diazotization is greatly decreased, and above 5° the diazonium salt begins to decompose.
8. Concentrating the solution below 1.7 l. results in markedly decreased purity.
9. If scratching does not succeed in inducing crystallization, a small portion of the solution may be removed and evaporated for seed.
10. According to the submitter, further purification can be effected by sublimation: the material is placed in the bottom of a Pyrex desiccator which is then evacuated and placed on a steam bath overnight. The mat of interwoven needles can be removed easily. One crystallization from [benzene](#) gives 37–40 g. (47–49%) of needles melting at 103–104°.

3. Discussion

[m-Hydroxybenzaldehyde](#) has been made by reduction of [m-hydroxybenzoic acid](#) with [sodium amalgam](#) in weak acid solution;¹ by oxidation of the arylsulfonic ester $\text{ArSO}_2\text{OC}_6\text{H}_4\text{CH}_3$ with [manganese dioxide](#) and [sulfuric acid](#) to the corresponding derivative of [m-hydroxybenzaldehyde](#) $\text{ArSO}_2\text{OC}_6\text{H}_4\text{CHO}$ and hydrolysis of the latter with concentrated [sulfuric acid](#);² from [m-dichloromethylphenyl benzoate](#) by heating with water and [calcium carbonate](#) under a pressure of 4–5 atm.³ The present method is derived from that of Tiemann and Ludwig⁴ and is similar to the procedure for the preparation of [m-chlorobenzaldehyde](#).⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 564](#)

References and Notes

1. Sandmann, *Ber.*, **14**, 969 (1881).
2. Ger. pat. 162,322 (*Chem. Zentr.*, **1905** II, 726).
3. Raschig, Ger. pat. 233,631 [*Chem. Zentr.*, **1911** I, 1388; *Frdl.*, **10**, 163 (1910–1912)].
4. Tiemann and Ludwig, *Ber.*, **15**, 2045 (1882); Rieche, *Ber.*, **22**, 2348 (1889); Ger. pat. 18,016 [*Frdl.*, **1**, 586 (1888)]; Subak, *Monatsh.*, **24**, 167 (1903).
5. [Org. Syntheses Coll. Vol. 2, 130 \(1943\)](#).

Appendix

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

sulfuric acid (7664-93-9)
hydrochloric acid (7647-01-0)
Benzene (71-43-2)
sodium nitrite (7632-00-0)
stannous chloride
calcium carbonate (471-34-1)
Norit (7782-42-5)
sodium (13966-32-0)
manganese dioxide (1313-13-9)
stannous chloride dihydrate (10025-69-1)
Benzaldehyde, m-hydroxy-,
m-Hydroxybenzaldehyde (100-83-4)
m-Chlorobenzaldehyde (587-04-2)
m-hydroxybenzoic acid (99-06-9)
m-Nitrobenzaldehyde (99-61-6)
m-aminobenzaldehyde (1709-44-0)
m-dichloromethylphenyl benzoate