



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.

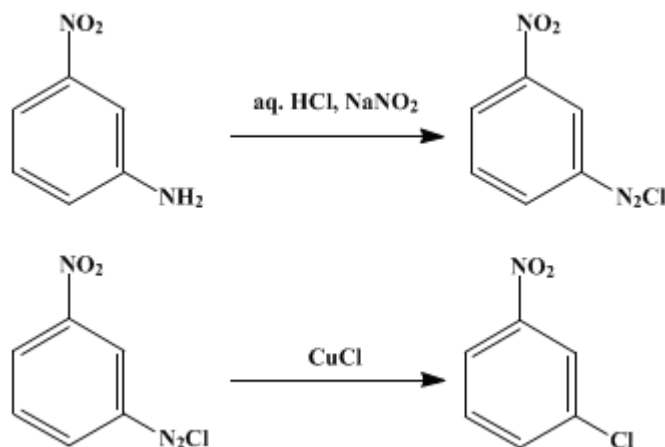
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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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## ***m*-CHLORONITROBENZENE**

[Benzene, 1-chloro-3-nitro-]



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### 1. Procedure

To a solution of 1200 g. (4.8 moles) of crystallized **copper sulfate** and 400 g. (6.9 moles) of **sodium chloride** in 4 l. of water at 60–70° is added a concentrated solution of 200 g. (1.7–1.8 moles) of (90–95 per cent) **sodium bisulfite** (prepared if desired by saturating a solution of 100 g. of **sodium carbonate** with **sulfur dioxide**). The white precipitate of **cuprous chloride** is filtered off, sucked dry as rapidly as possible, and suspended in a mixture of 2 l. of water and 1.5 l. of concentrated **hydrochloric acid** (sp. gr. 1.19) (**Note 1**).

In the meantime, 552 g. (4 moles) of good commercial ***m*-nitroaniline**, melting at 110° or above (**Note 2**), is dissolved in a mixture of 500 cc. of **hydrochloric acid** (sp. gr. 1.19) and 1 l. of hot water; 1100 cc. of **hydrochloric acid** (sp. gr. 1.19) is then added, and the solution is cooled rapidly, with stirring. It is then surrounded with a freezing mixture, and diazotized at a temperature below 1° by adding, with constant stirring, a solution of 288 g. (4 moles) of technical (95 per cent) **sodium nitrite** in 700 cc. of water, care being taken to avoid adding an excess over that necessary to produce a distinct reaction with starch-iodide paper (**p. 49**). This point is reached when all but about 25 cc. of the **nitrite** solution has been added; the addition requires about one and one-half hours. The cold solution is now filtered in order to remove some amorphous insoluble matter; this solid, when dry, weighs 50–55 g.

The clear filtrate, which has only a pale yellow color, is now run, with stirring, into the **cuprous chloride** solution in a 12-l. flask, while the temperature is kept at 25–30° (**Note 3**). A somewhat sticky precipitate first forms, which later becomes crystalline; **nitrogen** is evolved in a continuous stream. The addition requires about thirty minutes. The mixture is then warmed on a steam bath under an efficient reflux condenser until the evolution of **nitrogen** ceases. It is then distilled in a current of steam (using the apparatus described on **p. 479**) until no more **chloronitrobenzene** passed over; 9–10 l. of distillate collects during this process (**Note 4**). When quite cold, the water is decanted off, and the solid shaken with 1–2 l. of 1 per cent **sodium hydroxide** solution at 50°. The mixture is again allowed to cool, and the light yellow alkaline solution is decanted from the solid product, which is then collected on a filter, washed with a little cold water, dried, and distilled under reduced pressure. It boils completely at 116–117°/12 mm. or 124–125°/18 mm., and the distillate solidifies to a pale yellow solid which melts at 44–45° and weighs 430–450 g. (68–71 per cent of the theoretical amount).

### 2. Notes

1. It is more convenient to prepare [cuprous chloride](#) by reducing [copper sulfate](#) with [sodium bisulfite](#) than by the action of [copper](#) upon [cupric chloride](#). It is well to test a sample of the filtrate with [sodium bisulfite](#) solution; no further [cuprous chloride](#) should separate.

One mole of [cuprous chloride](#) should be used with one mole of diazonium salt. If less [cuprous chloride](#) is used the yield is decreased.

2. The yield will, of course, depend upon the quality of the [nitroaniline](#). The pure amine should yield none of the insoluble substance on diazotization, but the cost of purification would be prohibitive. It may be noted that if the weight of the insoluble residue be deducted, the yield amounts to 75–78 per cent of the theoretical amount.

3. It is important that the temperature should be held at 25–30° during the addition of the diazonium chloride to the [cuprous chloride](#) solution. At lower temperatures the decomposition of the unstable additive compound proceeds too slowly, and would cause too violent an evolution of [nitrogen](#) on warming; at higher temperatures the formation of tarry by-product increases.

4. If desired, the steam distillation may be omitted, since the proportion of non-volatile resinous impurities is very low. In this case the reaction mixture is allowed to cool, and the watery solution is decanted; the residue is then dissolved in 1–2 l. of [benzene](#), and the [benzene](#) solution washed with water and with dilute alkali, after which the solvent is removed by distillation on the steam bath and the residue distilled under reduced pressure. The yield and purity of the final product are equally satisfactory.

An iron condenser should not be used in the steam distillation of the crude *m*-chloronitrobenzene, as some reduction takes place and the yield is lowered by 10 to 15 per cent. The product is also deeply colored.

### 3. Discussion

*m*-Chloronitrobenzene can be prepared by the chlorination of [nitrobenzene](#) with the use of a catalyst such as [iodine](#),<sup>1</sup> [ferric chloride](#),<sup>2</sup> [antimony trichloride](#)<sup>3</sup> or [iron](#) and [iodine](#);<sup>4</sup> and from *m*-nitroaniline by diazotization.<sup>5</sup>

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### References and Notes

1. Laubenheimer, Ber. 7, 1765 (1874).
2. Varnholt, J. prakt. Chem. (2) 36, 25 (1887).
3. Beilstein and Kurbatov, Ann. 182, 102 (1876).
4. Fierz-David, Naturwissenschaften, 17, 13 (1929).
5. Griess, Jahresber. 423 (1863) and 457 (1866); Hollemann and Van Der Linden, Rec. trav. chim. 30, 317 (1911); Kohman, J. Phys. Chem. 29, 1052 (1925).

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### Appendix

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

[diazonium chloride](#)

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[sodium hydroxide](#) (1310-73-2)

[iron](#) (7439-89-6)

sodium chloride (7647-14-5)  
sodium carbonate (497-19-8)  
sulfur dioxide (7446-09-5)  
nitrogen (7727-37-9)  
copper sulfate (7758-98-7)  
sodium nitrite (7632-00-0)  
nitrite (14797-65-0)  
sodium bisulfite (7631-90-5)  
copper (7440-50-8)  
iodine (7553-56-2)  
Nitrobenzene (98-95-3)  
Benzene, 1-chloro-3-nitro-,  
m-Chloronitrobenzene (121-73-3)  
cuprous chloride (7758-89-6)  
chloronitrobenzene (88-73-3)  
cupric chloride (7758-89-6)  
nitroaniline  
ferric chloride (7705-08-0)  
antimony trichloride (7647-18-9)  
m-nitroaniline (99-09-2)