



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.

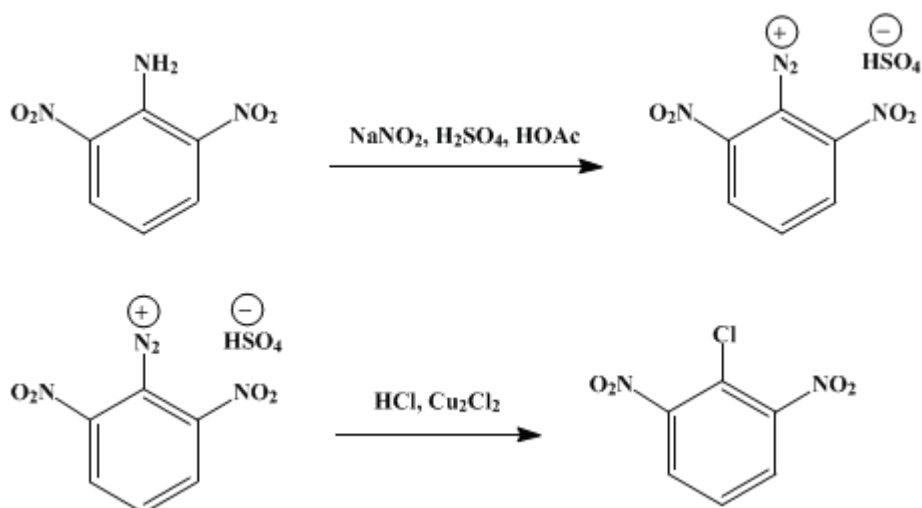
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1-CHLORO-2,6-DINITROBENZENE

[Benzene, 2-chloro-1,3-dinitro-]



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Checked by Arthur C. Cope, David J. Marshall, and Ronald M. Pike.

1. Procedure

Concentrated **sulfuric acid** (160 ml.) is placed in a 1-l. three-necked flask fitted with a glass stirrer and a thermometer, and 15.2 g. (0.22 mole) of solid **sodium nitrite** is added over a period of 10–15 minutes with stirring. After the addition is completed, the temperature is raised to 70° and the mixture is stirred until all the **sodium nitrite** dissolves. The solution is cooled to 25–30° with an ice bath, and a solution of 36.6 g. (0.2 mole) of **2,6-di-nitroaniline** (p.364) in 400 ml. of hot glacial **acetic acid** is added slowly, with stirring, at such a rate that the temperature remains below 40° (**Note 1**). After the addition is completed, the solution is stirred at 40° for 0.5 hour. A solution of 44 g. (0.44 mole) of **cuprous chloride** in 400 ml. of concentrated **hydrochloric acid** is prepared in a 2-l. beaker and cooled in an ice bath, and the solution of the diazonium salt is added in portions over a period of about 5 minutes, with manual stirring, at a rate which keeps the effervescence from becoming too vigorous. The mixture becomes hot during the addition, and it is stirred intermittently while being cooled in an ice bath until the effervescence slackens. It is then heated on a steam bath with occasional stirring until the temperature reaches 80°. After about 20 minutes at that temperature the effervescence ceases, and then an equal volume of water is added and the mixture is cooled in an ice bath. After several hours the yellow, crystalline **1-chloro-2,6-dinitrobenzene** is collected on a suction filter, washed with water, and dried (**Note 2**). The product, which is sufficiently pure for most purposes without recrystallization, is obtained in a yield of 28.7–30 g. (71–74%); m.p. 86–88°. The product can be recrystallized from 90% (by volume) **acetic acid** (2 ml. per g.) or by dissolving it in hot **benzene** (1.5 ml. per g.) and adding petroleum ether (3 ml. per g.); m.p. 86–87°.

2. Notes

1. The temperature of diazotization is critical. Lower yields are obtained if the temperature rises above 40°.
2. **1-Chloro-2,6-dinitrobenzene** is a skin irritant, and contact with it should be avoided.

3. Discussion

1-Chloro-2,6-dinitrobenzene has been prepared from **2,6-dinitroaniline** by the Sandmeyer

reaction,^{2,3,4} from 2,6-dinitrophenol and phosphorus oxychloride in the presence of N,N-diethylaniline,⁵ and from the mixture of isomers (in which 1-chloro-2,4-dinitrobenzene is present in largest amount) obtained by nitrating o-nitrochlorobenzene.^{3,6} The mixture of 2,4- and 2,6-dinitrochlorobenzene has been separated by the use of solution of sodium hydroxide in ethanol and water.⁷

References and Notes

1. The University, Glasgow, Scotland.
 2. Welsh, *J. Am. Chem. Soc.*, **63**, 3276 (1941).
 3. Hodgson and Dodgson, *J. Chem. Soc.*, **1948**, 1006.
 4. Gunstone and Tucker, *J. Appl. Chem. (London)*, **2**, 204 (1952).
 5. Boothroyd and Clark, *J. Chem. Soc.*, **1953**, 1504.
 6. Borsche and Rantscheff, *Ann.*, **379**, 152 (1911).
 7. Molard and Vaganay, *Mém. poudres*, **39**, 111 (1957) [*C. A.*, **52**, 19989 (1958)].
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Appendix

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

2,4- and 2,6-dinitro-chlorobenzene

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

sodium nitrite (7632-00-0)

Phosphorus Oxychloride (21295-50-1)

cuprous chloride (7758-89-6)

o-nitrochlorobenzene (88-73-3)

1-chloro-2,4-dinitrobenzene (97-00-7)

N,N-diethylaniline (91-66-7)

1-Chloro-2,6-dinitrobenzene,
Benzene, 2-chloro-1,3-dinitro- (606-21-3)

2,6-Dinitroaniline,

[2,6-di-nitroaniline \(606-22-4\)](#)

[2,6-dinitrophenol \(573-56-8\)](#)