



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.

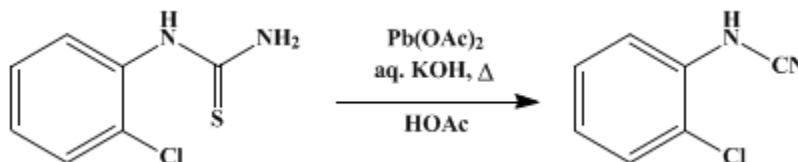
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***o*-CHLOROPHENYLCYANAMIDE**

[Carbanilonitrile, *o*-chloro-]



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Checked by Cliff S. Hamilton and David B. Capps.

1. Procedure

To a suspension of 37.4 g. (0.2 mole) of *o*-chlorophenylthiourea (p. 180) in 300 ml. of water at 100°, contained in a 3-l. beaker, is added a boiling solution of 132 g. (2 moles) of 85% potassium hydroxide in 300 ml. of water. The resulting solution is immediately treated with a hot saturated solution of 83.5 g. (0.22 mole) of lead acetate trihydrate, added as rapidly as possible and with good stirring (Note 1). The reaction mixture, from which large quantities of lead sulfide separate instantly, is boiled for 6 minutes and cooled to 0°, and the lead sulfide is filtered with suction by means of a large Büchner funnel (Note 2). The colorless filtrate is acidified at 0–5° (Note 3) by the slow addition with stirring of 120–140 ml. of glacial acetic acid. The white crystalline precipitate of nearly pure *o*-chlorophenylcyanamide which separates is collected by filtration on a suction filter and is washed with six 150-ml. portions of ice water. The crystalline mass of white plates is filtered, drained, and dried (Note 4). The yield of product, melting at 100–104°, is 26–28 g. (85–92%).

Recrystallization from benzene-light petroleum ether (8 ml. and 4 ml. respectively per gram of the dried precipitated material) gives lustrous needles of *o*-chlorophenylcyanamide, m.p. 105–106° (60–70% recovery) (Note 5). The above method is generally applicable and affords an excellent route to arylcyanamides (Note 6).

2. Notes

1. The exothermic reaction may cause the contents of the beaker to froth vigorously if the lead acetate solution is added too quickly. The reaction is readily controlled by adding the liquid in a rapid, thin stream with good stirring.
2. The use of a hardened filter paper or two thicknesses of ordinary filter paper is recommended. The black filter cake of lead sulfide may be extracted once again with 100 ml. of boiling 4% potassium hydroxide solution, and the extracts combined with the main filtrate.
3. The temperature of the solution is kept below 5° by the addition of suitable quantities of clean ice.
4. The product is sufficiently pure for use in further syntheses.
5. In benzene solution or in the solid state, *o*-chlorophenylcyanamide does not polymerize on storage for several months at 20–30°.
6. The desulfurization of arylthioureas can be used generally for preparing arylcyanamides in excellent yields. The submitter reports that α -naphthylcyanamide, melting at 124–128°, can be prepared in yields of 77–90% by this method.

3. Discussion

o-Chlorophenylcyanamide has been prepared by the action of lead acetate on *o*-chlorophenylthiourea.² The method is based on the analogous preparation of phenylcyanamide.³

References and Notes

1. University of London, London, England.
 2. Kurzer, *J. Chem. Soc.*, **1949**, 3033.
 3. Rathke, *Ber.*, **12**, 772 (1879); Krall et al., *J. Indian Chem. Soc.*, **19**, 343 (1942); **23**, 373 (1946).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

α -naphthylcyanamide

acetic acid (64-19-7)

Benzene (71-43-2)

lead sulfide

potassium hydroxide (1310-58-3)

lead acetate

phenylcyanamide

o-Chlorophenylthiourea (5344-82-1)

o-Chlorophenylcyanamide,
Carbanilonitrile, o-chloro- (45765-25-1)

lead acetate trihydrate