Organic Syntheses

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.

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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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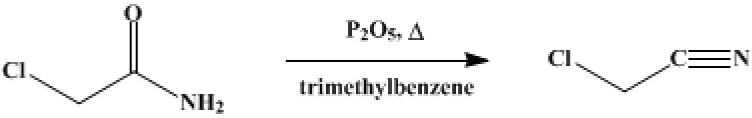
CHLOROACETONITRILE

[Acetonitrile, chloro-]



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1. Procedure

In a 3-l. round-bottomed three-necked flask fitted with an efficient mechanical stirrer, a reflux condenser, and a thermometer are placed 170 g. (1.2 moles) of phosphorus pentoxide, 187 g. (2 moles) of chloroacetamide[2] (Note 1), and 800 ml. of dry technical trimethylbenzene (Note 2). The mixture is refluxed gently with vigorous stirring for 1 hour. The reaction mixture is then allowed to cool to about 100° with continuous stirring, and the reflux condenser is replaced with a distilling adapter fitted with a thermometer and a water-cooled condenser.

The crude product and part of the solvent are distilled at atmospheric pressure (Note 3). The yield of crude product boiling at 124–128° is 121–131 g. (80–87%) (n_D^{25} 1.441–1.444). In order to obtain a pure product, the crude chloroacetonitrile is mixed with 10 g. of phosphorus pentoxide and redistilled through an efficient packed fractionating column (Note 4). The yield of pure chloroacetonitrile distilling at 123–124° is 93–106 g. (62–70%) (Note 5).

2. Notes

1. The practical grade of chloroacetamide obtainable from the Eastman Kodak Company can be used.
2. Technical trimethylbenzene with a boiling range of 166–174° is satisfactory.
3. About 200 ml. of solvent can be recovered. The remainder is left in the flask to facilitate removal of the residue.
4. A Fenske column packed with glass helices previously described in *Organic Syntheses*[3] is satisfactory. The product has n_D^{20} 1.426, d_4^{20} 1.1896, in good agreement with reported values.[4] When a Vigreux column was used the distillate had d_4^{20} 1.072 and n_D^{25} 1.430–1.436, indicating incomplete separation from the trimethylbenzenes (1,3,5-trimethylbenzene has d_4^{20} 0.86; n_D^{25} 1.494).
5. The product can also be distilled under reduced pressure; b.p. 60–61°/100 mm.; 30–32°/15 mm.

3. Discussion

Practical syntheses of chloroacetonitrile depend upon dehydration of chloroacetamide with phosphorus pentoxide. The present method uses a liquid reaction medium; in previous procedures the dry reagents were heated in the absence of solvent or liquid medium.[5,6]

References and Notes

1. University of Pennsylvania, Philadelphia, Pennsylvania.
2. *Org. Syntheses Coll. Vol.* **1**, 153 (1941).
3. *Org. Syntheses*, **25**, 2 (1945).
4. Rogers, *J. Am. Chem. Soc.*, **69**, 457 (1947).
5. School, *Ber.*, **29**, 2417 (1896).
6. Steinkopf, *Ber.*, **41**, 2540 (1908).

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

CHLOROACETAMIDE (79-07-2)

1,3,5-trimethylbenzene (108-67-8)

trimethylbenzene (526-73-8)

Chloroacetonitrile,
Acetonitrile, chloro- (107-14-2)

phosphorus pentoxide (1314-56-3)