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.

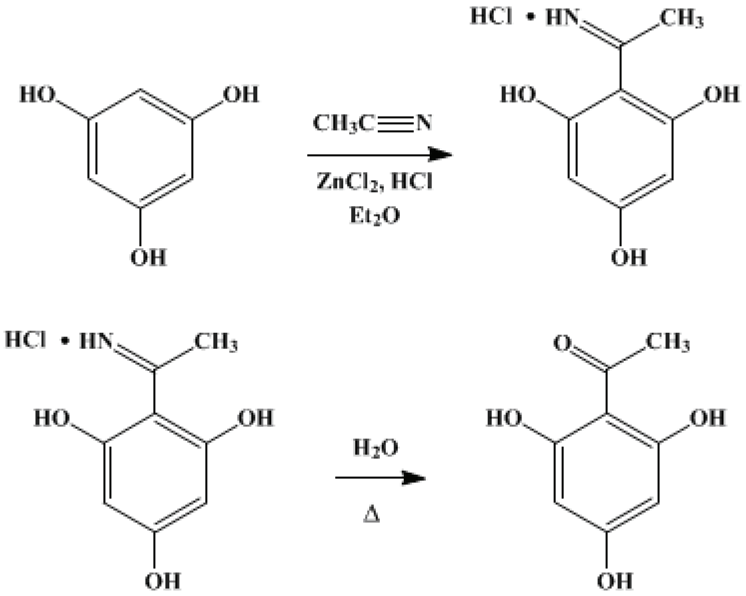
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

DOI:10.15227/orgsyn.015.0070

Organic Syntheses, Coll. Vol. 2, p.522 (1943); Vol. 15, p.70 (1935).

PHLOROACETOPHENONE



Submitted by K. C. Gulati, S. R. Seth, and K. Venkataraman.
Checked by John R. Johnson and M. T. Bush.

1. Procedure

In a 250-cc. filtering flask, fitted with a calcium chloride tube and a rubber stopper carrying an inverted thistle tube (Note 1) for the introduction of hydrogen chloride, are placed 20 g. (0.16 mole) of well-dried phloroglucinol (Note 2), 13 g. (0.32 mole) of anhydrous acetonitrile, 80 cc. of anhydrous ether, and 4 g. of finely powdered, fused zinc chloride. The flask is cooled in an ice-salt mixture and shaken occasionally while a rapid stream of dry hydrogen chloride is passed through the solution for two hours. The flask is allowed to stand in an ice chest for twenty-four hours, and hydrogen chloride is again passed into the mixture, now pale orange in color, for two hours. The flask is stoppered and allowed to stand in an ice chest for three days.

The bulky orange-yellow precipitate of the ketimine hydrochloride is separated by decanting the ether and washed twice with 20-cc. portions of dry ether. The solid is transferred to a 2-l. round-bottomed flask with 1 l. of hot water. The flask is provided with a reflux condenser, and the yellow solution is boiled vigorously over a wire gauze for two hours. About 3 to 4 g. of Norite is added; the solution is boiled for five minutes longer and filtered with suction while hot. The decolorizing carbon is extracted with two 100-cc. portions of boiling water and this filtrate added to the main portion.

After standing overnight the colorless or pale yellow needles of phloroacetophenone are filtered with suction and dried in an oven at 120° (Note 3). The yield is 20–23.5 g. (74–87 per cent of the theoretical amount) of a product which melts at 217–219° (corr.). This product is quite pure and may be used directly for many purposes. It may be recrystallized from thirty-five times its weight of hot water, with a loss of about 5 per cent. The recrystallized material melts at 218–219° (corr.).

2. Notes

1. A wide-mouthed entry tube for hydrogen chloride is necessary to avoid clogging due to separation of the solid ketimine hydrochloride.
2. All the reagents must be dried carefully. Phloroglucinol (Org. Syn. Coll. Vol. I, **1941**, 455) contains two molecules of water of hydration which is removed by drying overnight at 120°. The acetonitrile and ether used were freshly distilled from phosphorus pentoxide.

3. Phloroacetophenone crystallizes from aqueous solutions with one molecule of water of hydration.[1] The oven-dried crystals take up water readily on exposure to the air. Phloroacetophenone gives a wine-red color with ferric chloride in contrast to the violet color given by phloroglucinol.[2]

3. Discussion

The Hoesch reaction is the most satisfactory method for preparing phloroacetophenone.[3] The procedure described above is that of Robinson and Venkataraman.[4] Phloroacetophenone has been obtained also by the action of acetyl chloride on phloroglucinol in the presence of aluminum chloride.[2]

References and Notes

1. Gulati, Seth, and Venkataraman, J. Chem. Soc. **1934**, 1766.
2. Shriner and Kleiderer, J. Am. Chem. Soc. **51**, 1269 (1929).
3. Hoesch, Ber. **48**, 1129 (1915).
4. Robinson and Venkataraman, J. Chem. Soc. **1926**, 2347.

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

Phloroacetophenone

hydrogen chloride (7647-01-0)

ether (60-29-7)

acetonitrile (75-05-8)

acetyl chloride (75-36-5)

decolorizing carbon,
Norite (7782-42-5)

aluminum chloride (3495-54-3)

zinc chloride (7646-85-7)

ferric chloride (7705-08-0)

Phloroglucinol (108-73-6)

phosphorus pentoxide (1314-56-3)

ketimine hydrochloride

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved