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.

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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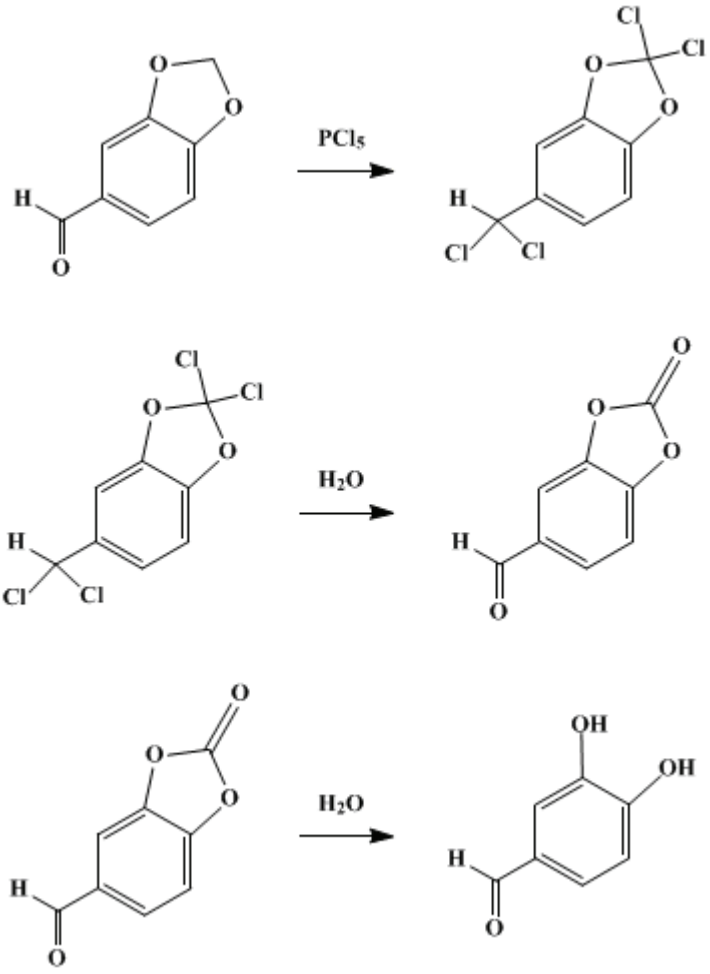
PROTOCATECHUALDEHYDE



Submitted by Johannes S. Buck and F. J. Zimmermann.
Checked by Reynold C. Fuson and W. E. Ross.

1. Procedure

To 108 g. (0.72 mole) of piperonal in a 3-l. round-bottomed flask is added, in portions of 20 to 30 g., 454 g. (2.18 moles) of fresh phosphorus pentachloride. The reaction is vigorous at first, and the flask is kept cold with ice; moisture must be excluded. After about half of the pentachloride has been added the reaction becomes sluggish and cooling is unnecessary. The entire addition requires about thirty minutes. The resulting green or blue liquid containing undissolved pentachloride is heated very gently over a flame for about sixty minutes to expel hydrogen chloride. From the turbid, light brown liquid thus formed, volatile material is removed on a steam bath under the reduced pressure of a water pump. This operation takes about thirty minutes. The contents of the flask are then poured into 5 l. of cold water contained in a 12-l. round-bottomed flask (Note 1). A milky oil is formed which rises and sinks in the water and, after about thirty minutes, becomes solid. After standing overnight, the mixture is boiled gently for three hours. The brown solution, containing a little tar, is cleared with charcoal and evaporated under reduced pressure to about 700 cc., when the aldehyde begins to separate. The solution is allowed to stand overnight at about 0°; a large crop of crystals separates, is collected on a filter, and washed with a little water. The product is purified by recrystallization from three times its weight of water. It melts at 153–154°, with decomposition, and weighs 61 g. (61 per cent of the theoretical amount).

2. Notes

1. This must be done cautiously because the residual phosphorus pentachloride reacts vigorously with water.

3. Discussion

Protocatechualdehyde has been made by a variety of methods, but is usually prepared from catechol by the Reimer-Tiemann method;[1] from vanillin[2] or veratric aldehyde[3] by demethylation; and from piperonal by the action of aluminum chloride[4] or phosphorus pentachloride followed by hydrolysis.[5]

References and Notes

1. Reimer and Tiemann, Ber. **9**, 1268 (1876); Tiemann and Koppe, ibid. **14**, 2015 (1881).
2. Tiemann and Haarmann, ibid. **7**, 620 (1874).
3. Dreyfus, Ger. pat. 193,958 [Frdl. **9**, 161 (1908–10)].
4. Givaudan-Delawanna, Inc., U. S. pat. 2,027,148 [C. A. **30**, 1395 (1936)].
5. Fittig and Remsen, Ann. **159**, 144 (1871); Pauly, Ber. **40**, 3096 (1907); Barger, J. Chem. Soc. **93**, 563 (1908); Hoering and Baum, Ber. **41**, 1914 (1908).

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

hydrogen chloride (7647-01-0)

phosphorus pentachloride (10026-13-8)

aluminum chloride (3495-54-3)

Catechol (120-80-9)

veratric aldehyde (120-14-9)

vanillin (121-33-5)

piperonal (120-57-0)

PROTOCATECHUALDEHYDE (139-85-5)