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.

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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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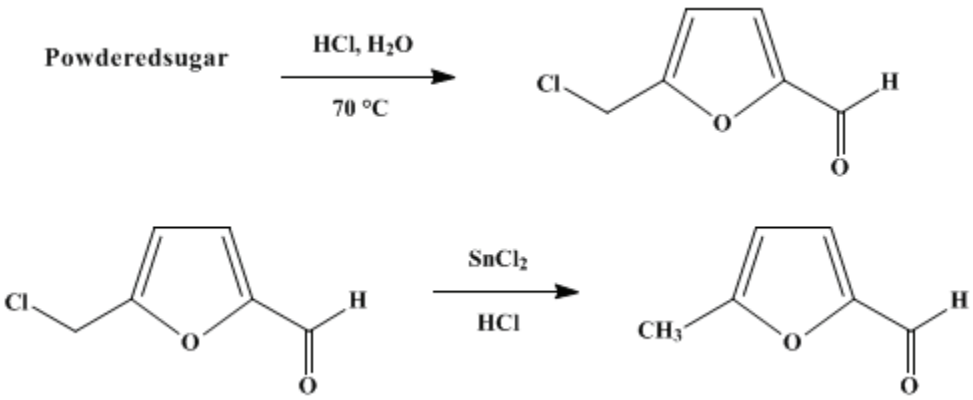
5-METHYLFURFURAL

[2-Furaldehyde, 5-methyl-]



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1. Procedure

In a 12-l. round-bottomed flask, fitted with a cork bearing a thermometer and a large bent glass tube, is placed 6 l. of 32 per cent hydrochloric acid (sp. gr. 1.163) (Note 1). The acid is heated to 50°, and 1 kg. (2.9 moles) of powdered sugar (Note 2) is dissolved in the liquid with shaking. The dark-colored solution is heated rapidly to 70–72°, kept at this temperature for ten minutes, and poured at once onto 3 kg. of cracked ice in a large earthenware crock (preferably in a hood) (Note 3). When the mixture has cooled to room temperature, 600 g. (2.67 moles) of commercial stannous chloride crystals ($SnCl_2 \cdot 2H_2O$) is added. The reaction mixture is stirred thoroughly for ten minutes and then allowed to stand for twenty-four hours.

The following day the acid liquid is filtered with suction through a large Büchner funnel, to remove large quantities of humus which are produced. The humus on the filter is washed with two 350-cc. portions of water and finally with two 300-cc. portions of benzene. The filtered liquid and aqueous washings have a volume of approximately 10 l. The 5-methylfurfural is removed from the aqueous layer by extraction with benzene, using three 300-cc. portions of the solvent for each 2 l. of liquid (Note 4). The combined benzene extracts (about 5 l.) are divided into two or three portions; each is washed with two 150-cc. portions of 5 per cent sodium carbonate solution and two 100-cc. portions of water. The benzene solution is dried with 100–150 g. of anhydrous magnesium or sodium sulfate, and the benzene is removed by distillation from a 1-l. flask provided with a short fractionating column and a separatory funnel for the continuous introduction of the solution. The distillation is stopped when the temperature of the distilling vapor reaches 85°.

The residue is transferred to a 250-cc. Claisen flask; two small portions of benzene (5–10 cc.) are used to rinse the last drops of the residue into the flask. The last traces of benzene are removed by warming gently under reduced pressure, and the 5-methylfurfural is then collected at 83–85°/15 mm. (Note 5). The yield is 63–70 g. (20–22 per cent of the theoretical amount, based upon the levulose portion of the sugar) (Note 6).

2. Notes

1. Commercial hydrochloric acid gives as satisfactory results as the chemically pure grade. The concentration of the hydrochloric acid should not exceed 32 per cent (sp. gr. 1.163) since stronger acid causes frothing during the heating and gives somewhat lower yields (56–57 g.).
2. Ordinary confectioners' sugar (XXXX sugar) was used. The 3 per cent of starch which it contains has

no harmful effect.
3. Lengthening the time of heating or raising the temperature above 72° is definitely harmful.
4. The extractions should be carried out immediately after filtration since further quantities of humus are deposited if the liquid is allowed to stand.
5. 5-Methylfurfural discolors rapidly on standing, and after some time becomes quite black. The usual antioxidants do not retard this alteration perceptibly.
6. 5-Methylfurfural may be prepared by a modification of this method, which is more rapid but gives lower yields.[1] A solution of 800 g. of sucrose in 1 l. of hot water is allowed to flow slowly into a boiling solution of 500 g. of stannous chloride crystals, 2 kg. of sodium chloride, and 4 l. of 12 per cent sulfuric acid in a 12-l. flask. The aldehyde distils as rapidly as it is formed and is steam-distilled from the original distillate after being rendered alkaline with sodium carbonate. The product is isolated by benzene extraction of the second distillate and distillation under reduced pressure. The yield is 27–35 g. (10–13 per cent of the theoretical amount).

3. Discussion

5-Methylfurfural has been prepared by the distillation of rhamnose with dilute mineral acids[2] and by the reduction of 5-bromo- and 5-chloromethylfurfural with stannous chloride.[3] The above procedure, starting from sucrose, has been published by Rinkes.[4]

References and Notes

1. Scott and Johnson, J. Am. Chem. Soc. **54**, 2553 (1932).
2. Maquenne, Ann. chim. phys. (6) **22**, 91 (1891); Runde, Scott, and Johnson, J. Am. Chem. Soc. **52**, 1288 (1930).
3. Fenton and Gostling, J. Chem. Soc. **79**, 811 (1901).
4. Rinkes, Rec. trav. chim. **49**, 1123 (1930); **52**, 337 (1933).

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

starch

magnesium or sodium sulfate

5-bromo- and 5-chloromethylfurfural

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

stannous chloride

sucrose

5-Methylfurfural,
2-Furaldehyde, 5-methyl- (620-02-0)

levulose (57-48-7)

rhamnose