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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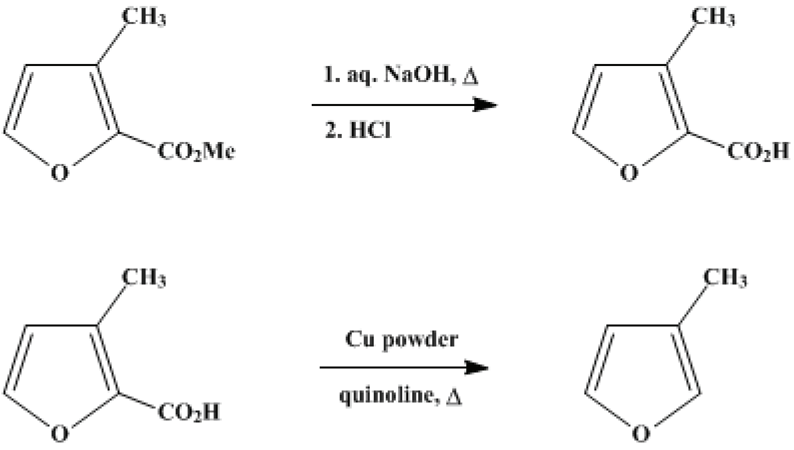
3-METHYL-2-FUROIC ACID AND 3-METHYLFURAN

[2-Furoic acid, 3-methyl-]

[Furan, 3-methyl-]



Submitted by D. M. Burness[1]
Checked by James Cason and Robert B. Hutchison.

1. Procedure

A. *3-Methyl-2-furoic acid*. A mixture of 35 g. (0.25 mole) of methyl 3-methyl-2-furoate (p.649) and 80 ml. of aqueous 20% sodium hydroxide is heated under reflux for 2 hours. The solution is cooled, acidified with about 50 ml. of concentrated hydrochloric acid (sp. gr. 1.18), stirred vigorously for a few minutes to ensure freeing of the acid from its salt, then cooled to room temperature before the product is collected by suction filtration. The product is washed with about 25 ml. of water used in two portions, drained well on the funnel, then dried. The yield of essentially pure 3-methyl-2-furoic acid is 28.5–29.5 g. (90–93%), m.p. 134–135° (Note 1).

B. *3-Methylfuran*. A mixture of 25 g. of 3-methyl-2-furoic acid, 50 g. of quinoline (Note 2), and 4.5 g. of copper powder is placed in a 125-ml. round-bottomed flask attached by a ground joint to a 30-cm. simple Vigreux column which delivers to a water-cooled condenser. The condenser is connected to a small distilling flask which serves as receiver, with the tip of the condenser extending to the edge of the bulb of the flask. The receiver is cooled in an ice-salt bath (Note 3). The round-bottomed flask is heated by means of an electric mantle or liquid bath.

When the quinoline is heated to boiling by raising the bath temperature to about 250°, carbon dioxide is evolved at a moderate rate; the reaction is usually completed in 2–3 hours. Near the end of the reaction, heat is increased to about 265°, and the last distillate is collected until the temperature at the top of the column begins to rise rapidly above 65°. The contents of the receiver are decanted from any ice present and dried over about 1.5 g. of anhydrous magnesium sulfate, followed by Drierite, in a tightly closed flask. Redistillation yields 13.5–14.5 g. (83–89%) of colorless 3-methylfuran, b.p. 65.5–66°, n_{D}^{25} 1.4295–1.4315 (Note 4) and (Note 5).

2. Notes

1. In a run thirty times the size described, the submitter obtained a yield of 85%.
2. The quinoline should be dried by distillation from anhydrous barium oxide.
3. For larger runs, the side arm of the distilling flask should be attached to a cold trap immersed in an ice-salt bath, for about 10% of the product is likely to pass through the first receiver.

4. The product turns yellow on standing, even overnight. It can be stabilized with 0.1% hydroquinone or similar material.[2]

5. The submitter obtained similar results in runs about twenty times the size described. Over-all yields for the four steps starting with 4,4-dimethoxy-2-butanone (p.649) were consistently in the range 50–55%.

3. Discussion

3-Methyl-2-furoic acid has been prepared by the oxidation of 3-methyl-2-furaldehyde[3] and by the degradation of 3-methyl-2-isovalerylfuran (Elsholtzia ketone).[4] 3-Methylfuran has been prepared by the present method[5] and more recently by a three-step method starting with methallyl chloride and ethyl orthoformate.[6] Circuitous routes from citric acid[7] and malic acid[8] have also been used.

References and Notes

1. Eastman Kodak Co., Rochester, New York.
2. Cass, U. S. pat. 2,489,265 (1949, to du Pont) [*C. A.*, **44**, 1543 (1950)].
3. Reichstein, Zschokke and Goerg, *Helv. Chim. Acta*, **14**, 1277 (1931).
4. Asahina and Murayama, *Arch. Pharm.*, **252**, 442 (1914); Asahina, *Acta phytochim. (Japan)*, **2**, 12 (1924) [*Chem. Zentr.*, **1924, II**, 1694].
5. Burness, *J. Org. Chem.*, **21**, 102 (1956); U. S. pat. 2,772,295 [*C. A.*, **51**, 7424 (1957)].
6. Cornforth, *J. Chem. Soc.*, **1958**, 1310.
7. Rinkes, *Rec. trav. chim.*, **50**, 1127 (1931); Reichstein and Zschokke, *Helv. Chim. Acta*, **14**, 1270 (1931).
8. Gilman and Burtner, *J. Am. Chem. Soc.*, **55**, 2903 (1933).

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

Drierite

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

citric acid (77-92-9)

hydroquinone (123-31-9)

barium oxide

carbon dioxide (124-38-9)

copper powder (7440-50-8)

Ethyl orthoformate

Quinoline (91-22-5)

magnesium sulfate (7487-88-9)

malic acid (617-48-1)

3-Methyl-2-furoic acid,
2-Furoic acid, 3-methyl- (4412-96-8)

3-Methylfuran,
Furan, 3-methyl- (930-27-8)

Methyl 3-methyl-2-furoate (6141-57-7)

4,4-dimethoxy-2-butanone (5436-21-5)

3-methyl-2-furaldehyde

3-methyl-2-isovalerylfuran

methallyl chloride (563-47-3)