



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.

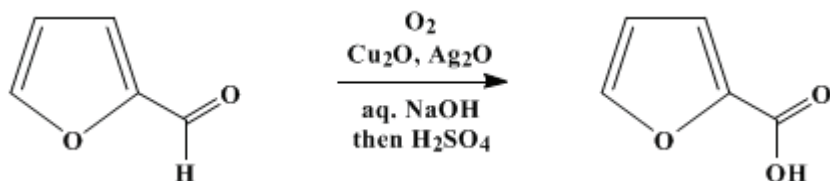
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 4, p.493 (1963); Vol. 36, p.36 (1956).

2-FUROIC ACID



Submitted by R. J. Harrisson and M. Moyle¹.

Checked by James Cason and W. N. Baxter.

1. Procedure

A 1-l. flask (Note 1) is fitted with a condenser, an efficient stirrer, two dropping funnels, a thermometer extending well into the flask, and a delivery tube which extends far enough to be below the surface of the stirred liquid.

To the flask is added 250 ml. of a 2.5% solution of sodium hydroxide and a cuprous oxide-silver oxide catalyst (Note 2). In the two dropping funnels are placed, respectively, 96 g. (1.0 mole) of furfural (Note 3) and a solution of 40 g. (1.0 mole) of sodium hydroxide in 100 ml. of water. The contents of the flask are heated to about 55°, vigorous stirring is started, and a rapid stream of oxygen is bubbled through as the contents of the two funnels are added simultaneously (Note 4) to the reaction mixture at such a rate (20–25 min.) as to maintain the temperature at 50–55° (Note 5) without external heating. After the additions have been completed, vigorous stirring and passage of oxygen are continued until the temperature drops below 40° (15–30 min., depending on the rate of oxygen flow).

The catalyst is separated by filtration, and the aqueous solution is extracted with three 30-ml. portions of ether (Note 6), acidified with 30% sulfuric acid, boiled for 45 min. (Note 7) with 6–7 g. of carbon, then filtered hot. The filtrate is cooled to 0° and allowed to stand at this temperature for 1 hour or longer. The 2-furoic acid, which separates as pale pink needles, m.p. 130–132°, is collected by suction filtration and washed with small portions of ice water (Note 8). The yield is 96–101 g. (86–90%).

2. Notes

1. Since oxygen is passed through the solution at 55°, it is best to operate under a reflux condenser. Ground joint fittings are not essential but convenient. The checkers used a 4-necked flask with ground joints; the thermometer was hung through the condenser, and one neck was arranged for attachment of the gas delivery tube and one of the separatory funnels.
2. The catalyst used is commercial cuprous oxide (9.6 g., 10% of the weight of the furfural) and commercial silver nitrate (0.5 g., 0.5% of the weight of the furfural) in 15 ml. of water. The cuprous oxide is suspended in the rapidly stirred 2.5% sodium hydroxide solution, and the solution of silver nitrate is added to give a dark brown suspension of cuprous oxide and silver oxide which is used directly. So long as oxygen is being passed through the reaction mixture, the life of the catalyst appears to be unlimited.
3. A sample of commercial furfural is purified by simple distillation or steam distillation immediately before use. The submitters have carried out this reaction on an 8-mole scale following the same procedure except that a total reaction time of about 4 hours was required.
4. The simultaneous addition of furfural and sodium hydroxide maintains the concentration of sodium hydroxide at about 2.5%, at which concentration only a small percentage of furfuryl alcohol is formed in the accompanying Cannizzaro reaction.
5. Below 50°, the reaction is too slow; above 55°, the reaction becomes violent and cooling becomes necessary. Frothing may be checked by addition of small amounts of benzene.
6. Ether extraction at this stage removes furfuryl alcohol (about 12 g.). If this is not removed, the reaction mixture becomes resinous on acidification and heating.

7. During the period of boiling in acid solution a small amount of polymeric material forms, and this is separated when the charcoal is removed by filtration.
8. The solubility of 2-furoic acid in water is 2.8 g. per 100 ml. at 0°; however, its solubility in the salt solution resulting from the reaction is quite low. Usually it is not possible to obtain further material from the filtrate by salting out with sodium chloride; however, in case a lowered yield is obtained in the first crop it may be profitable to investigate the possibility of obtaining additional material from the filtrate.

3. Discussion

2-Furoic acid has been made by oxidation of lactose followed by pyrolysis, by the oxidation of 2-acetylfuran, 2-methylfuran, or furfuryl alcohol using potassium ferricyanide in alkaline medium, and by other methods already listed.² In addition, furfural has been oxidized to furoic acid by air in the presence of sodium hydroxide and silver nitrate,³ by hydrogen peroxide in the presence of pyridine or picoline,⁴ by sodium or potassium hypochlorite,⁵ by means of sodium hydroxide in methanol or sodium hydroxide in methanol followed by hydrogen peroxide,⁶ and by sodium hydroxide in the presence of a copper oxide-silver oxide-carbon catalyst.⁷

References and Notes

1. University of Sydney, Sydney, Australia.
2. *Org. Syntheses Coll. Vol. 1*, 276 (1941).
3. Taniyama, *Toho-Reiyon Kenkyû Hôkoku*, **2**, 51 (1955) [*C. A.*, **53**, 4247 (1959)].
4. Baba, *Kagaku Kenkyusho Hôkoku*, **33**, 168 (1957) [*C. A.*, **52**, 7267 (1958)]; Physical and Chemical Researches, Inc. (by Midorikawa and Baba), Jap. pat. 6113 (1959) [*C. A.*, **54**, 1544 (1961)].
5. Farbenfabriken Bayer A.-G., Ger. pat. 908,023 [*C. A.*, **52**, 10201 (1958)]; Arita and Odawara (to Asahi Chemical Industries Co.), Jap. pat. 1130 (1950) [*C. A.*, **47**, 2214 (1953)].
6. Kuwada et al. (to Nippon Petroleum Oil Co.), Jap. pat. 3730 (1951) [*C. A.*, **47**, 8096 (1953)].
7. Terai et al. (to Noguchi Research Institute, Inc.), Jap. pat. 1111 (1951) [*C. A.*, **47**, 3883 (1953)].

Appendix

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

sulfuric acid (7664-93-9)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

silver oxide (20667-12-3)

silver nitrate (7761-88-8)

oxygen (7782-44-7)

carbon (7782-42-5)

pyridine (110-86-1)

cuprous oxide

hydrogen peroxide (7722-84-1)

2-Furoic acid,
furoic acid (88-14-2)

copper oxide (1317-38-0)

Furfural (98-01-1)

Furfuryl alcohol (98-00-0)

sodium hypochlorite (7681-52-9)

potassium hypochlorite

potassium ferricyanide (13746-66-2)

picoline (109-06-8)

lactose

2-acetylfuran (1192-62-7)

2-methylfuran (534-22-5)