



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.

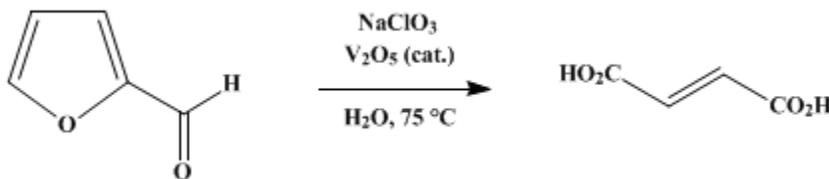
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior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

Organic Syntheses, Coll. Vol. 2, p.302 (1943); Vol. 11, p.46 (1931).

FUMARIC ACID



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1. Procedure

A 5-l. flat-bottomed flask, equipped with a long (80–90 cm.) widebore condenser, a separatory funnel, and a mechanical stirrer (Note 1), is supported 10 cm. above an electric hot plate. Two grams of vanadium pentoxide (Note 2), 450 g. (4.2 moles) of sodium chlorate, and 1 l. of water are placed in the flask; the stirrer is started, the mixture is heated to 70–75° (Note 3), and about 5–10 cc. of 200 g. (2.06 moles) of furfural (Note 4) is added. As soon as a vigorous reaction starts the balance of the furfural is added rapidly enough to maintain it (Note 5). The entire addition requires seventy to eighty minutes. Then the mixture is heated at 70–75°, with stirring, for ten to eleven hours and allowed to stand overnight at room temperature. The crude fumaric acid is filtered with suction and dried in the air. It weighs 155–170 g. (65–72 per cent of the theoretical amount) (Note 6).

More fumaric acid may be obtained from the filtrate by heating it on the water bath with 50 cc. of concentrated hydrochloric acid; the solution usually turns blue at the end of the reaction. The solution is concentrated to about 700 cc. and then cooled with running water. The fumaric acid which separates is collected on a filter and dried in the air. It weighs 10–15 g. and melts at 282–284° in a sealed tube.

The crude product is purified by recrystallization from about 1250 cc. of 1 *N* hydrochloric acid. This gives 100–110 g. of pure fumaric acid, melting at 282–284° in a sealed tube. An additional amount of the acid may be obtained by concentrating the filtrate to a small volume on a water bath. The total yield of pure fumaric acid is 120–138 g. (50–58 per cent of the theoretical amount).

2. Notes

- The yields were lower when mechanical stirring was not used.
- The catalyst is prepared by suspending 20 g. of c.p. ammonium metavanadate in 200 cc. of water and adding slowly 30 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The reddish brown semicolloidal precipitate is washed several times with water by decantation and finally suspended in 300 cc. of water and allowed to stand at room temperature for three days. This treatment makes the precipitate granular and easy to filter. The precipitate is collected on a filter using a pump and washed several times with water to free it from hydrochloric acid. It is then dried at 120° for twelve hours, finely powdered, and again dried for twelve hours at 120°.
- To observe the temperature, a thermometer may be suspended in the flask through the inner tube of the condenser. The mixture may be heated first to 70–75° over a free flame.
- The furfural used was the technical grade furnished by the Miner Laboratories, Chicago. According to these laboratories the furfural was "about 99 per cent pure." The crude furfural obtained as described in *Org. Syn. Coll. Vol. I, 1941, 280* may be used.
- The reaction does not seem to start immediately upon the addition of the first few cubic centimeters of furfural. When the vigorous reaction commences, the temperature rises to about 105° and remains there for some time. The yield of fumaric acid seems to depend somewhat upon the rapidity of this stage of the reaction. It is therefore necessary to regulate the addition of furfural so that a vigorous reaction is maintained.
- The crude fumaric acid is from 74 to 78 per cent pure as found by titration with standard alkali. The

only impurity present besides inorganic salts is a little [sodium hydrogen maleate](#) which is decomposed by the [hydrochloric acid](#) during the purification process.

3. Discussion

[Fumaric acid](#) has been prepared from [bromosuccinic acid](#) by heating with water,¹ or dilute [hydrobromic acid](#),² and by heating the acid above its melting point.³ It has also been prepared by heating [malic acid](#),⁴ by isomerization of [maleic acid](#),⁵ and by the reduction of [tartaric acid](#) with [phosphorus](#) and [iodine](#).⁶ The procedure described is the most satisfactory for laboratory use, and is a slight modification of one described in the literature.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 177](#)
- [Org. Syn. Coll. Vol. 2, 553](#)

References and Notes

1. Volhard, *Ann.* **268**, 256 (1892); Müller and Suckert, *Ber.* **37**, 2598 (1904).
2. Fittig, *Ann.* **188**, 90 (1877).
3. Kekulé, *ibid.* **130**, 22 (1864); Volhard, *ibid.* **242**, 158 (1887).
4. Lassaigne, *Ann. chim. phys.* (2) **11**, 93 (1819); Pelouze, *Ann.* **11**, 265 (1834); Wislicenus, *ibid.* **246**, 91 (1888); Michael, *J. prakt. Chem.* (2) **46**, 231 (1892); Jungfleisch, *Bull. soc. chim.* (2) **30**, 147 (1878).
5. Wislicenus, *Ber.* **29**, 1080 (abstracts) (1896); Ciamician and Silber, *ibid.* **36**, 4267 (1903); Skraup, *Monatsh.* **12**, 107 (1891); Weiss and Downs, *J. Am. Chem. Soc.* **44**, 1119 (1922); Terry and Eichelberger, *ibid.* **47**, 1402 (1925).
6. Phelps, *Ger. pat.* 254,420 [*Frld.* **11**, 99 (1912–14)]; *Org. Chem. Reagents II*, Univ. Illinois Bull. **18** (6), 35 (1920).
7. Milas, *J. Am. Chem. Soc.* **49**, 2007 (1927); Buluigina, *Masloboino-Zhirovoe Delo* **1934**, No. 4, 43 [*C. A.* **30**, 1743 (1936)].

Appendix

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

[hydrochloric acid](#) (7647-01-0)

[ammonium metavanadate](#) (7803-55-6)

[HYDROBROMIC ACID](#) (10035-10-6)

[PHOSPHORUS](#) (7723-14-0)

[vanadium pentoxide](#)

[maleic acid](#) (110-16-7)

[iodine](#) (7553-56-2)

sodium chlorate (7775-09-9)

tartaric acid (87-69-4)

Fumaric acid (110-17-8)

Furfural (98-01-1)

sodium hydrogen maleate (3105-55-3)

bromosuccinic acid (923-06-8)

malic acid (617-48-1)