



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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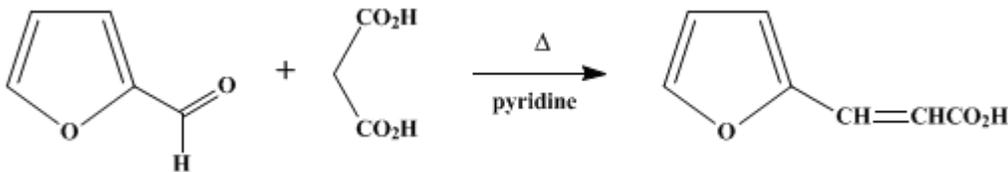
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.425 (1955); Vol. 25, p.51 (1945).

FURYLACRYLIC ACID

[2-Furanacrylic acid]

[I. METHOD A]



Submitted by S. Rajagopalan and P. V. A. Raman.

Checked by C. S. Hamilton and R. A. Alberty.

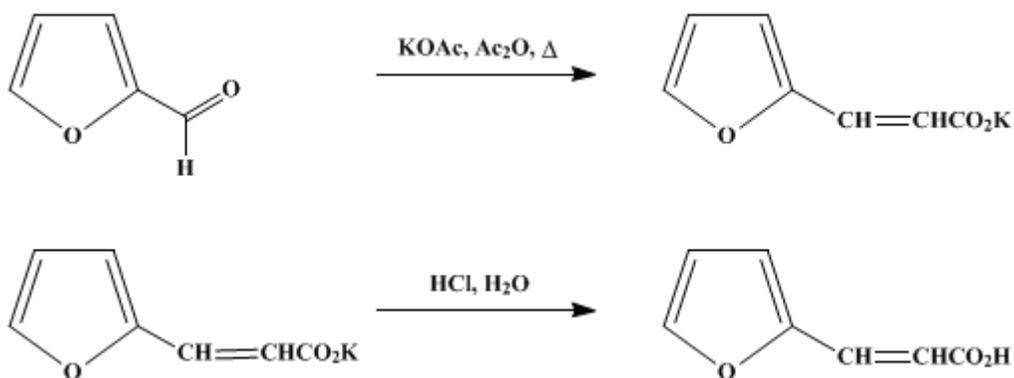
1. Procedure

In a 1-l. round-bottomed flask fitted with a reflux condenser are placed 192 g. (166 ml., 2 moles) of freshly distilled [furfural](#) (Note 1), 208 g. (2 moles) of [malonic acid](#) (Note 2), and 96 ml. (1.2 moles) of [pyridine](#) (Note 3). The flask is heated on a boiling water bath for 2 hours, and the reaction mixture is cooled and diluted with 200 ml. of water. The acid is dissolved by the addition of concentrated aqueous [ammonia](#), the solution is filtered through a fluted filter paper, and the paper is washed with three 80-ml. portions of water. The combined filtrates are acidified with an excess of diluted (1:1) [hydrochloric acid](#) with stirring. The mixture is cooled by running water and then allowed to stand in an ice bath for at least 1 hour. The [ferylacrylic acid](#) is filtered, washed with four 100-ml portions of water, and dried. The yield of practically colorless needles melting at 141° is 252–254 g. (91–92%). If a purer product is desired, recrystallization is best effected from dilute alcohol (Note 4). On slow cooling of the solution, needles melting at 141° separate.

2. Notes

1. Commercial [furfural](#) is subjected to a single distillation; b.p. $160\text{--}161^\circ$.
2. Commercial [malonic acid](#) is dried at 100° for 2 hours and stored in a stoppered bottle.
3. The [pyridine](#), which may be a commercial grade, is dried over sticks of [potassium hydroxide](#) for a few hours and filtered.
4. A convenient procedure is to dissolve the acid in a slight excess of 50% [ethanol](#), reflux the solution with charcoal (5 g. per 100 g. of acid) for 5–10 minutes, and filter through a fluted filter in a preheated funnel. Any solid material that separates toward the later stages is redissolved by the addition of a few drops of [ethanol](#). The residue is thoroughly washed with boiling water. The hot solution is then diluted with cold water until crystals separate, heated to boiling, cooled slowly, and allowed to stand in a refrigerator for several hours. When the mother liquors are used for subsequent batches, the usual loss (2–3%) by recrystallization is more than halved.

[II. METHOD B]



Submitted by John R. Johnson
 Checked by R. L. Shriner and C. M. Stevens.

1. Procedure

In a 3-l. round-bottomed flask provided with a mechanical stirrer and a 90-cm. air-cooled condenser are placed 288 g. (3 moles) of freshly distilled [furfural](#), 460 g. (425 ml., 4.5 moles) of [acetic anhydride](#), and 294 g. (3 moles) of dry, pulverized, freshly fused [potassium acetate](#) ([Note 1](#)). The ingredients are mixed thoroughly, stirring is started, and the flask is heated in an oil bath at 150° (bath temperature) for 4 hours, without interruption ([Note 2](#)). It is well to make provision for [acetic acid](#) vapor which escapes through the air condenser.

After cooling slightly, the reaction mixture is transferred to a large flask and treated with 3.5 l. of water. Part of this is used to rinse out the reaction flask. The mixture is boiled with 30 g. of [Norit](#) for about 10 minutes and is filtered while still *hot* with suction, using a preheated Büchner funnel. [Furylacrylic acid](#) tends to separate quickly and sometimes offers trouble in clogging the funnel. The filtrate is acidified to Congo red by the addition of a 1:1 solution of concentrated [hydrochloric acid](#) in water. After being cooled to 20° or below, preferably with stirring, and being allowed to stand for at least 1 hour, the acid is filtered with suction and washed with a small quantity of ice water. The yield is 270–290 g. (65–70%). The light tan crude acid melts at $138\text{--}139^\circ$ ([Note 3](#)).

2. Notes

1. If fused [sodium acetate](#) is used the reaction is slower and 6–8 hours' heating is required.
2. When the temperature of the bath approaches $145\text{--}150^\circ$ a rapid exothermic reaction sets in. This must be controlled (by application of cold, wet towels to the flask) to avoid too vigorous ebullition.
3. [Furylacrylic acid](#) melting at $138\text{--}139^\circ$ is sufficiently pure for most purposes. The acid is perfectly white when pure, but many recrystallizations are required to attain that state. It may be recrystallized from [benzene](#) or ligroin ($90\text{--}100^\circ$) with the addition of [Norit](#). The loss is about 20–25%, and the product melts at $139\text{--}140^\circ$ (sometimes $140\text{--}141^\circ$).

3. Discussion

This acid is usually prepared by the condensation of [furfural](#) with [malonic acid](#) in the presence of [pyridine](#).¹ It may also be prepared from [furfural](#) by the Perkin reaction.² The use of [potassium acetate](#) is advantageous since it allows the reaction to proceed rapidly at relatively lower temperatures. A preparation from [furfuralacetone](#) by oxidation has also been reported.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 742](#)
- [Org. Syn. Coll. Vol. 4, 302](#)

References and Notes

1. Dutt, *J. Indian Chem. Soc.*, **1**, 297 (1925); Kurien, Pandya, and Surange; *J. Indian Chem. Soc.*, **11**, 824 (1934) [*C. A.*, **29**, 3325 (1935)].
 2. Marckwald, *Ber.*, **10**, 357 (1877); Gibson and Kahnweiler, *Am. Chem. J.*, **12**, 314 (1890).
 3. Hurd and Thomas, *J. Am. Chem. Soc.*, **55**, 1646 (1933).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ligroin

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

Benzene (71-43-2)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

Norit (7782-42-5)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

Furfural (98-01-1)

furfuralacetone

Furylacrylic acid,
2-Furanacrylic acid (539-47-9)

Malonic acid (141-82-2)

potassium acetate (127-08-2)