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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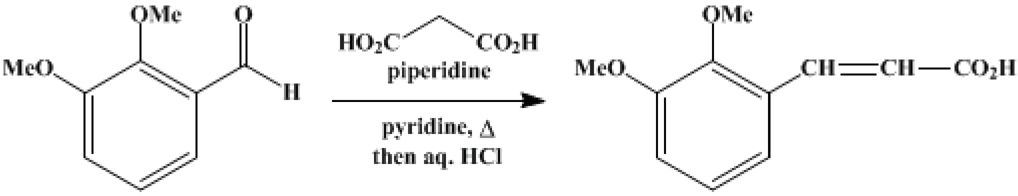
*Organic Syntheses, Coll. Vol. 4, p.327 (1963); Vol. 31, p.35 (1951).*

# 2,3-DIMETHOXYCINNAMIC ACID

## [Cinnamic acid, 2,3-dimethoxy-]



Submitted by J. Koo, M. S. Fish, G. N. Walker, and J. Blake[1].
Checked by T. L. Cairns and A. E. Barkdoll.

## 1. Procedure

In a 3-l. round-bottomed flask (Note 1), fitted with a reflux condenser and a thermometer, are placed 208 g. (2 moles) of malonic acid (Note 2) 166 g. (1 mole) of 2,3-dimethoxybenzaldehyde (Note 3), and 400 ml. of pyridine. The malonic acid is dissolved by shaking and warming on a steam bath (Note 4). Piperidine (15 ml.) is then added, the reflux condenser and thermometer are fitted into place (Note 5), and the mixture is heated to 80°. About 30 minutes should be allowed for this rise in temperature. An internal temperature of 80–85° is maintained for 1 hour, and the material is finally heated under reflux (109–115°) for an additional 3 hours (Note 6).

After being cooled the reaction mixture is poured into a large beaker containing 4 l. of cold water. The mixture is acidified by slowly adding with stirring 500 ml. of concentrated hydrochloric acid; it should be strongly acidic at this point. The light-brown crystals are separated by suction filtration and washed 4 times with 150-ml. portions of cold water. The crude acid is dissolved in a solution of 80 g. of sodium hydroxide in 3 l. of water. The resulting is filtered, diluted with an additional 1.2 l. of water, and acidified by adding with stirring 600 ml. of 1:1 hydrochloric acid. The mixture is filtered, and the crystalline material is washed with three 150-ml. portions of cold water. The product is dried at 60–70° (Note 7). The yield is 180–205 g. (87–98%), m.p. 174–178° (Note 8). Further purification is usually not necessary, but it may be accomplished by recrystallization from methyl ethyl ketone, using 12 ml. of solvent per gram of acid. The hot solution is filtered rapidly through a steam-heated Büchner funnel and chilled for several hours. A recovery of 70% of product, m.p. 179–180°, may be obtained.

## 2. Notes

1. A large flask is preferred to ensure against possible loss by foaming.
2. An excess of malonic acid is necessary for high yields. An equimolecular amount of malonic acid results in yields as low as 50%.
3. A practical grade of 2,3-dimethoxybenzaldehyde gives satisfactory results. It is convenient to weigh and transfer this material as a liquid.
4. If the malonic acid is not in solution before addition of the piperidine, the reaction cannot be controlled properly. It is advisable to heat the mixture to 50° to effect solution.
5. The thermometer may be suspended in the mixture through the condenser by means of a long wire.
6. Evolution of carbon dioxide begins at about 55–60°. The prescribed temperatures are necessary to prevent undue foaming.
7. The product should be dried to constant weight in an oven. Drying for several days is usually required.
8. This method is a general one. It can be used with a variety of substituted aromatic aldehydes.

## 3. Discussion

2,3-Dimethoxycinnamic acid has been prepared by heating 2,3-dimethoxybenzaldehyde with acetic anhydride and sodium acetate at 200°[2] and by the condensation of 2,3-dimethoxybenzaldehyde and ethyl acetate with sodium, followed by hydrolysis.[3] The present preparation represents an adaption of the Doebner reaction.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 731

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## References and Notes

1. University of Pennsylvania, Philadelphia, Pennsylvania.
2. von Krannichfeldt, *Ber.*, **46**, 4021 (1913).
3. Perkin and Robinson, *J. Chem. Soc.*, **105**, 2387 (1914).

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

hydrochloric acid (7647-01-0)

ethyl acetate (141-78-6)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

carbon dioxide (124-38-9)

pyridine (110-86-1)

sodium (13966-32-0)

piperidine (110-89-4)

Malonic acid (141-82-2)

methyl ethyl ketone (78-93-3)

2,3-Dimethoxycinnamic acid,
Cinnamic acid, 2,3-dimethoxy- (7461-60-1)

2,3-dimethoxybenzaldehyde (86-51-1)