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.

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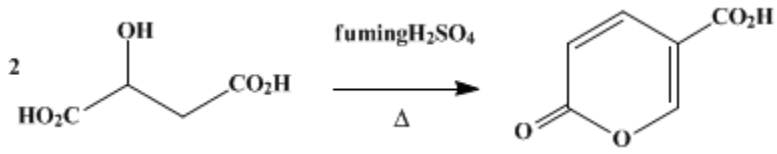
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.031.0023

Organic Syntheses, Coll. Vol. 4, p.201 (1963); Vol. 31, p.23 (1951).

COUMALIC ACID



Submitted by Richard H. Wiley and Newton R. Smith[1,2].
Checked by C. F. H. Allen and George A. Reynolds.

1. Procedure

In a 2-l. round-bottomed flask are placed 200 g. (1.49 moles) of powdered malic acid (Note 1) and 170 ml. of concentrated sulfuric acid. To this suspension are added three 50-ml. portions of 20–30% fuming sulfuric acid at 45-minute intervals. After the evolution of gas has slackened, the solution is heated on a water bath for 2 hours with occasional shaking. The reaction mixture is then cooled and poured slowly onto 800 g. of crushed ice with stirring. After standing 24 hours, the acid is filtered on a Büchner funnel, washed with three 50-ml. portions of ice-cold water, and dried on a water bath. The yield of crude acid, melting at 195–200°, is 75–80 g. (Note 2) and (Note 3).

One-half of the crude product is dissolved in five times its weight of hot methanol, and the solution is boiled with 3 g. of Norit or decolorizing carbon. The solution is filtered while hot and cooled in an ice bath. The precipitate is collected on a filter and washed with 25 ml. of cold methanol. The mother liquors are used to recrystallize the remaining crude material. The yield of bright yellow coumalic acid, melting at 206–209°, is 68–73 g. (65–70%) (Note 4).

2. Notes

1. A technical free-flowing powder, melting at 126–128°, was used.
2. This washing is essential to remove the mineral acid and to avoid partial esterification that otherwise takes place during the methanol recrystallization step.
3. The submitters state that an additional 10–12 g. of crude acid can be obtained from the filtrate by extraction with ether in a continuous extractor.
4. Depending on the color of the crude acid, several additional recrystallizations may be required to obtain a colorless product.

3. Discussion

This procedure is essentially that of von Pechmann.[3] Esters of coumalic acid may be obtained by heating the sulfuric acid solution with the appropriate alcohol.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 532
- Org. Syn. Coll. Vol. 5, 982

References and Notes

1. University of Louisville, Louisville, Kentucky.
2. The submitters wish to thank the Research Corporation for a grant under which this work was done.
3. von Pechmann, *Ann.*, **264**, 272 (1891).
4. Campbell and Hunt, *J. Chem. Soc.*, **1947**, 1176; Gilman and Burtner, *J. Am. Chem. Soc.*, **55**, 2903

(1933); Ruzicka, *Helv. Chim. Acta*, **4**, 504 (1921).

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

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

carbon,
Norit (7782-42-5)

malic acid (617-48-1)

Coumalic acid (500-05-0)