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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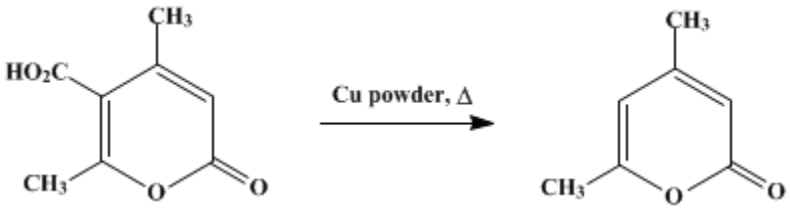
4,6-DIMETHYLCOUMALIN

[Sorbic acid, 5-hydroxy-3-methyl, δ-lactone]



Submitted by Newton R. Smith and Richard H. Wiley[1,2].
Checked by R. S. Schreiber and H. H. Fall.

1. Procedure

In a 125-ml. Claisen flask, equipped with a capillary for vacuum distillation and a thermometer, are placed 50 g. (0.3 mole) of isodehydroacetic acid (p. 549) and 2 g. of copper powder (Note 1). A 125-ml. simple distilling flask, cooled by a water jet, is used as a vacuum receiver and is attached to a water aspirator. The Claisen flask is heated at atmospheric pressure in an oil bath at 230–235° for 45 minutes or until the decarboxylation has ceased. The pressure on the system is then slowly reduced, and the dimethylcoumalin is distilled directly from the reaction flask (Note 2). The crude dimethylcoumalin (34–35 g., 92–95%) is redistilled from a Claisen flask. The yield of 4,6-dimethylcoumalin is 30–32 g. (81–87%); b.p. 140–142°/35 mm. (Note 3); m.p. 50–51°.

2. Notes

1. Copper chromite catalyst may be substituted.
2. The submitters recommend 3 hours for decarboxylation. At 45-minute intervals the pressure on the system is reduced and the dimethylcoumalin distilled directly from the reaction flask. After the distillation slackens, the pressure is returned to atmospheric and the decarboxylation is continued. However, the checkers found that the decarboxylation is virtually completed during the first 45-minute period.
3. The checkers observed a boiling point of 134–136°/35 mm. for 4,6-dimethylcoumalin. The melting point, however, was identical with that reported by the submitters.

3. Discussion

4,6-Dimethylcoumalin has been prepared by the decarboxylation of isodehydroacetic acid in sulfuric acid or by heating,[3] and by the distillation of 4-methyl-2-pyrone-6-acetic acid.[4]

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. Hantzsch, *Ann.*, **222**, 17 (1883).
4. Rice and Vogel, *Chem. & Ind. (London)*, **1959**, 992.

Appendix

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

4,6-Dimethylcoumalin

Isodehydroacetic acid

sulfuric acid (7664-93-9)

copper powder (7440-50-8)

COPPER CHROMITE

Sorbic acid, 5-hydroxy-3-methyl, δ-lactone (675-09-2)

dimethylcoumalin

4-methyl-2-pyrone-6-acetic acid