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.

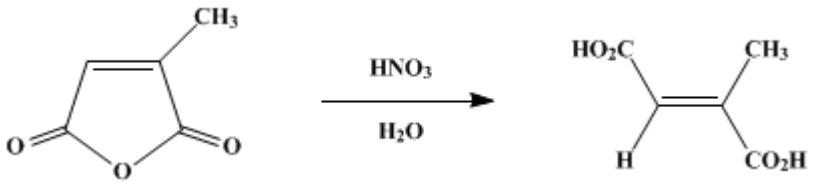
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

DOI:10.15227/orgsyn.011.0074

Organic Syntheses, Coll. Vol. 2, p.382 (1943); Vol. 11, p.74 (1931).

MESACONIC ACID



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1. Procedure

A mixture of 100 g. (0.89 mole) of citraconic anhydride (Note 1) 100 cc. of water, and 150 cc. of dilute nitric acid (1 part of concentrated nitric acid to 4 parts of water by volume) is evaporated in a 500-cc. Erlenmeyer flask until the appearance of red fumes (Note 2). The solution is cooled and the mesaconic acid is collected on a filter. The mother liquor is evaporated to 150 cc., cooled, and the crystalline solid which separates is collected on a filter. Further concentration of the mother liquor to 50 cc. yields more product (Note 3). The entire product is recrystallized from 100 cc. of water. The yield of mesaconic acid melting at 203–205° is 50–60 g. (43–52 per cent of the theoretical amount).

2. Notes

1. An equivalent amount of citraconic acid can be used. Directions for preparing citraconic acid and anhydride are given on p. 140.
2. It is necessary to carry the evaporation to the point where red fumes appear in order for the rearrangement to take place. The volume is usually about 250 cc.
3. The concentration of the mother liquor must be carried out in steps in order to obtain an efficient separation of mesaconic acid.

3. Discussion

Mesaconic acid has been prepared by heating citraconic acid with dilute nitric acid,[1] with hydriodic acid,[2] or with concentrated sodium hydroxide solution;[3] by heating a concentrated water solution of itaconic or citraconic acid at 180–200°;[4] by treating citradibromopyrotartaric acid and mesodibromopyrotartaric acid with potassium iodide and copper at 150°;[5] and by heating citraconic anhydride with nitric acid.[6]

References and Notes

1. Gottlieb, Ann. **77**, 268 (1851).
2. Kekulé, Ann. Spl. **2**, 94 (1862).
3. Delisle, Ann. **269**, 82 (1892).
4. Swarts, Jahresb. **1873**, 579.
5. Swarts, Zeit. für Chem. **1868**, 259.
6. Fittig and Landolt, Ann. **188**, 73 (1877).

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

citraconic acid and anhydride

itaconic or citraconic acid

citradibromopyrotartaric acid

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

potassium iodide (7681-11-0)

copper (7440-50-8)

hydriodic acid (10034-85-2)

Citraconic anhydride (616-02-4)

Citraconic acid (498-23-7)

Mesaconic acid (498-24-8)

mesodibromopyrotartaric acid