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.

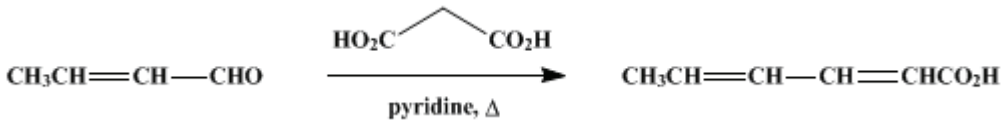
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.024.0092

Organic Syntheses, Coll. Vol. 3, p.783 (1955); Vol. 24, p.92 (1944).

SORBIC ACID



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1. Procedure

A mixture of 80 g. (93.2 ml., 1.14 moles) of crotonaldehyde (b.p. 102–103°), 120 g. (1.15 moles) of malonic acid (m.p. 134–135°), and 120 g. (122 ml., 1.52 moles) of pyridine (b.p. 113–115°) is heated for 3 hours in a 1-l. flask on a steam bath under a reflux condenser. At the end of this period the evolution of carbon dioxide will have practically ceased. The flask and contents are then cooled in ice, and a solution of 42.5 ml. (0.76 mole) of concentrated sulfuric acid in 100 ml. of water is added with shaking. Most of the sorbic acid separates at once; the remainder is obtained by chilling the solution in an ice bath for 3 hours. The crude acid is filtered by suction and washed once with a small amount of ice water; it is recrystallized at once from 250 ml. of boiling water. The purified acid, which separates on standing overnight in the ice chest, is filtered; it melts at 134°. The yield is 36–41 g. (28–32%) (Note 1), (Note 2), and (Note 3).

2. Notes

1. The submitters have found that the percentage yield is the same when double the above quantities are used.
2. This is an example of a general reaction. If acetic acid is used as a solvent, the substituted malonic acids can be secured, whereas organic bases facilitate the loss of carbon dioxide. The product is generally a mixture from which but a single substance can be isolated.
3. The use of simple aldehydes gives better yields of unsaturated acids; this is especially noticeable when aromatic aldehydes are employed.[1] Mixtures of α,β- and β,γ-unsaturated acids have been reported when aliphatic aldehydes and certain basic catalysts are used.[2,3]

3. Discussion

Sorbic acid has been prepared from crotonaldehyde[4] or aldol[5] and malonic acid in pyridine solution; by hydrogen peroxide oxidation of the condensation product of crotonaldehyde and pyruvic acid;[6] and by the action of alkali on 3-hydroxy-4-hexenoic acid,[7,8] β,δ-disulfo-*n*-caproic acid,[9] parasorbic acid,[10,11] and 3,5-hexadienoic acid.[12]

References and Notes

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

aldol

parasorbic acid

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

carbon dioxide (124-38-9)

pyridine (110-86-1)

hydrogen peroxide (7722-84-1)

Malonic acid (141-82-2)

Pyruvic acid (127-17-3)

crotonaldehyde (123-73-9)

Sorbic acid (110-44-1)

3-hydroxy-4-hexenoic acid

3,5-hexadienoic acid

β,δ-disulfo-n-caproic acid