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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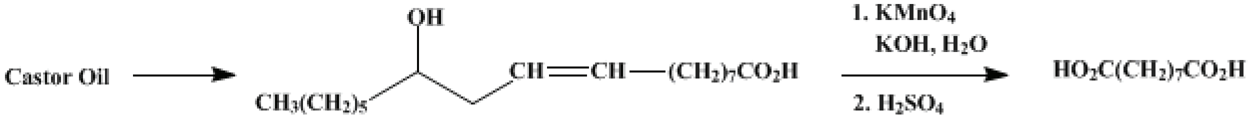
# AZELAIC ACID



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## 1. Procedure

Five hundred grams of castor oil (Note 1) is added to a solution of 100 g. of potassium hydroxide in 1 l. of 95 per cent alcohol. The mixture is placed in a 3-l. flask equipped with a reflux condenser and is boiled for three hours. The solution is then poured into 3 l. of water and acidified by the addition of a solution of 100 cc. of concentrated sulfuric acid in 300 cc. of water. The acid which separates is washed twice with warm water, shaken intermittently for one hour with 100 g. of anhydrous magnesium sulfate, and then filtered with suction. The yield of crude ricinoleic acid thus obtained is 480 g. The acid should be oxidized at once (Note 2).

Two hundred and forty grams (0.8 mole) of the dried ricinoleic acid is dissolved in 1.6 l. of water containing 64 g. of potassium hydroxide. A 12-l. round-bottomed flask is equipped with a powerful mechanical stirrer, and in it are placed 625 g. (3.5 moles) of potassium permanganate and 7.5 l. of water at 35°. The mixture is stirred to facilitate solution of the permanganate, and, if necessary, heat is applied to maintain the temperature at 35°. When the permanganate has completely dissolved, the alkaline solution of ricinoleic acid is added in a single portion with vigorous stirring (Note 3). The temperature rises rapidly to about 75°. Stirring is continued for a half hour, or until a test portion added to water shows no permanganate color.

The oxidation mixture is now divided into two equal portions and each portion is treated as follows: To the mixture is added a solution of 200 g. of concentrated sulfuric acid in 600 cc. of water (Note 4). The mixture is heated on a steam bath for 15 minutes to coagulate the manganese dioxide which is filtered while still very hot (Note 5). After filtration the manganese dioxide is placed in a 4-l. beaker and boiled with 2 l. of water to dissolve any azelaic acid that may adhere to it. This mixture is filtered while hot, and the filtrate is added to the main portion.

The combined filtrates and washings for the two portions of the oxidation mixture are evaporated to a volume of about 4 l., and this solution is cooled in ice. The crystals which separate are filtered with suction, washed once with cold water, and dried. The yield is 70–80 g. of material having a melting point that may vary from 95 to 105°.

The crude substance is dissolved in 1.2 l. of boiling water, filtered with suction, and allowed to cool. The crystals are filtered, washed with water, and dried. There is obtained 48–55 g. of product (32–36 per cent of the theoretical amount, based upon the amount of crude ricinoleic acid taken for oxidation). The melting point of the purified azelaic acid is 104–106°.

## 2. Notes

1. The castor oil used was a commercial grade designated as "Crystal." It was obtained from the Baker Castor Oil Company, New York City.
2. If ricinoleic acid is allowed to stand, polymerization occurs; Baker and Ingold report[1] that the polymerized acid gives very poor yields in the oxidation by nitric acid.
3. At this point the mixture tends to froth quite badly, and, if stirring is not vigorous, material may be lost. Addition of a small quantity of ether or benzene may be resorted to but is unnecessary if stirring is efficient.
4. The acid must be added slowly and carefully to prevent too rapid evolution of carbon dioxide with

consequent foaming. If possible, each of the two portions should be placed in a large container, such as a 12-l. flask.
5. For this purpose it is advisable to use three 20-cm. Büchner funnels supported in 2-l. filter flasks.

## 3. Discussion

Azelaic acid can be prepared by the oxidation of castor oil with nitric acid;[2] by the oxidation of ricinoleic acid with nitric acid[1] and with alkaline permanganate;[3] by the oxidation of methyl oleate with alkaline permanganate;[4] by the ozonization of oleic acid and decomposition of the ozonide;[5] by the ozonization of methyl ricinoleate and decomposition of the ozonide;[6] by the action of carbon dioxide upon 1,7-heptamethylenemagnesium bromide;[7] by the hydrolysis of 1,7-dicyanoheptane;[8] and by the oxidation of dihydroxystearic acid with dichromate and sulfuric acid, the dihydroxy acid being prepared from oleic acid and hydrogen peroxide.[9]

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## References and Notes

1. Baker and Ingold, J. Chem. Soc. **123**, 128 (1923); Verkade, Rec. trav. chim. **46**, 137 (1927).
2. Arppe, Ann. **120**, 288 (1861); **124**, 86 (1862); Dale and Schorlemmer, ibid. **199**, 144 (1879); Kiliani, Ber. **54**, 469 (1921); Day, Kon, and Stevenson, J. Chem. Soc. **117**, 642 (1920); Böeseken and Lutgerhorst, Rec. trav. chim. **51**, 164 (1932).
3. Maquenne, Bull. soc. chim. (3) **21**, 1061 (1899).
4. Armstrong and Hilditch, J. Soc. Chem. Ind. **44**, 43T (1925).
5. Harries and Tank, Ber. **40**, 4556 (1907); Rieche, Ger. pat. 565,168 [C. A. **27**, 1008 (1933)].
6. Haller and Brochet, Compt. rend. **150**, 500 (1910).
7. v. Braun and Sobecki, Ber. **44**, 1926 (1911).
8. Dionneau, Ann. chim. (9) **3**, 249 (1915).
9. Bennett and Gudgeon, J. Chem. Soc. **1938**, 1679.

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

ozonide

1,7-heptamethylenemagnesium bromide

alcohol (64-17-5)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

nitric acid (7697-37-2)

potassium permanganate (7722-64-7)

carbon dioxide (124-38-9)

potassium hydroxide (1310-58-3)

hydrogen peroxide (7722-84-1)

manganese dioxide (1313-13-9)

Azelaic acid (123-99-9)

magnesium sulfate (7487-88-9)

ricinoleic acid

methyl oleate (112-62-9)

oleic acid (112-80-1)

methyl ricinoleate (141-24-2)

1,7-dicyanoheptane (1675-69-0)

dihydroxystearic acid