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.
**n-HEPTANOIC ACID**

[Enanthic acid]

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1. Procedure

In a 5-l. flask, fitted with a mechanical stirrer and cooled in an ice bath, are placed 2.7 l. of water and 350 cc. (644 g.) of concentrated sulfuric acid (sp. gr. 1.84). When the temperature has fallen to 15°, 342 g. (403 cc., 3 moles) of heptaldehyde (Note 1) is added, followed by 340 g. (2.15 moles) of potassium permanganate in 15-g. portions. The permanganate is added at such a rate that the temperature does not rise above 20° (Note 2). When the addition of the permanganate is complete, sulfur dioxide is passed through the solution until it becomes clear (Note 3). The oily layer is separated, washed once with water, and distilled from a modified Claisen flask having a 30-cm. fractionating side arm. The fore-runs are separated from any water and distilled again; this is followed by a redistillation of the high-boiling fractions. The yield of material boiling at 159–161°/100 mm. is 296–305 g. (76–78 per cent of the theoretical amount) (Note 4). This product is sufficiently pure for many purposes; titration indicates a purity of 95–97 per cent.

For further purification the product is dissolved in a solution of 140 g. (3.5 moles) of sodium hydroxide in 700 cc. of water and steam-distilled from a 2-l. flask until a test portion of the distillate is free of oil. The solution remaining in the flask is cooled to room temperature and acidified with 375 cc. (4.5 moles) of concentrated hydrochloric acid. The heptanoic acid is separated and distilled from a Claisen flask with fractionating side arm. The recovery of acid boiling at 155–157°/80 mm. is 85–90 per cent of the weight of impure material used. Titration indicates it to be 100 per cent pure.

2. Notes

1. Freshly distilled heptaldehyde boiling at 85.5–87.5°/90 mm. was used.
2. The stirring must be vigorous. About two hours is required for the addition of the permanganate.
3. Sulfur dioxide, in the presence of sulfuric acid, reduces the precipitated manganese dioxide to the soluble sulfate; the removal of this large quantity of flocculent material greatly facilitates separation of the heptanoic acid. The addition of sulfur dioxide requires about two hours; an excess is to be avoided. Sodium bisulfite may be used if sulfur dioxide is not available.
4. Occasionally the heptanoic acid has a yellow color which cannot be removed by fractionation.

3. Discussion

Heptanoic acid has been prepared by the oxidation of heptaldehyde with nitric acid,¹ with potassium permanganate in alkaline aqueous solution² or in acetone solution,³ or with potassium dichromate and sulfuric acid;⁴ and by carbonating the reaction product of sodium and 1-chlorohexane.⁵

References and Notes

1. Tilley, Ann. 67, 107 (1848); Mehlis, ibid. 185, 360 (1877); Krafte, Ber. 15, 1717 (1882).
3. Rogers, J. Am. Pharm. Assoc. 12, 503 (1923) [C. A. 18, 152 (1924)].

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

- sulfuric acid (7664-93-9)
- hydrochloric acid (7647-01-0)
- sodium hydroxide (1310-73-2)
- nitric acid (7697-37-2)
- potassium permanganate (7722-64-7)
- sulfur dioxide (7446-09-5)
- sodium bisulfite (7631-90-5)
- acetone (67-64-1)
- sodium (13966-32-0)
- manganese dioxide (1313-13-9)
- potassium dichromate (7778-50-9)

- Enanthic acid,
- Heptanoic acid,
- n-HEPTANOIC ACID (111-14-8)

- 1-chlorohexane (544-10-5)
- heptaldehyde (111-71-7)