



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.

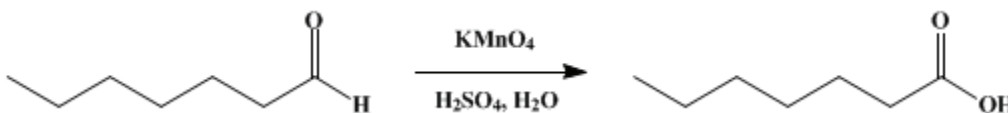
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.315 (1943); Vol. 16, p.39 (1936).

***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); Krafft, *Ber.* **15**, 1717 (1882).
2. Fournier, *Bull. soc. chim.* (4) **5**, 921 (1909).
3. Rogers, *J. Am. Pharm. Assoc.* **12**, 503 (1923) [*C. A.* **18**, 152 (1924)].

4. Grimshaw and Schorlemmer, Ann. **170**, 141 (1873).
 5. Morton, LeFevre, and Hechenbleikner, J. Am. Chem. Soc. **58**, 754 (1936).
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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)