



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](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.

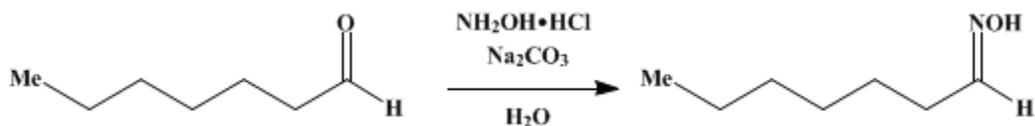
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 2, p.313 (1943); Vol. 11, p.54 (1931).*

## HEPTALDOXIME

[Enanthaldehyde oxime]



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### 1. Procedure

In a 5-l. two-necked flask, fitted with a mechanical stirrer, a reflux condenser, a thermometer, and a separatory funnel, are placed an aqueous solution of 348 g. (5 moles) of [hydroxylamine hydrochloride](#) (*Org. Syn. Coll. Vol. I, 1941, 318*) in 600 cc. of cold water and 460 g. (4 moles) of [heptaldehyde](#) (*Note 1*). Stirring (*Note 2*) is started, and a solution of 265 g. (2.5 moles) of anhydrous c.p. [sodium carbonate](#) in 500 cc. of water is added at such a rate that the temperature of the reaction mixture does not rise above 45°. Stirring is continued at room temperature for an hour after the addition of the [sodium carbonate](#) solution is complete.

The oily layer on top of the reaction mixture is separated and washed with two 100-cc. portions of water (*Note 3*). The washed product is transferred to a 1.5-l. modified Claisen flask and distilled under reduced pressure from an oil bath. The first fraction contains a very small amount of water along with a mixture of [heptanonitrile](#) and heptaldoxime. The product is collected at 103–107°/6 mm. (temperature of the oil bath, 140–147°) (*Note 4*). The yield is 420–480 g. (81–93 per cent of the theoretical amount). The product solidifies slowly on cooling and melts at 44–46°. It can be used for reduction to *n*-[heptylamine](#) (p. 318) without further purification.

The product can be purified by recrystallization from 60 per cent [ethyl alcohol](#), using approximately 70 cc. of the solvent to 25 g. of the distilled product. One such recrystallization (*Note 5*) gives white leaflets melting at 53–55° (*Note 6*) and (*Note 7*). The yield of recrystallized material from a single run is 315–320 g.

### 2. Notes

1. The [heptaldehyde](#) used boiled at 54–59°/16 mm.
2. Since the [heptaldehyde](#) and the aqueous solution of [hydroxylamine hydrochloride](#) form a heterogeneous mixture, it is necessary to provide rapid, efficient stirring in order to obtain good results. [Ethyl alcohol](#) can be used to provide a homogeneous solution, but the yield seems to be diminished slightly owing to the presence of more high-boiling material.
3. The product is so insoluble in water that an ether extraction is hardly necessary to obtain all the product from the water solution if sufficient time is allowed for the separation of the two layers.
4. The temperature of the oil bath during distillation is important. The first fraction is cut as soon as a constant boiling point is reached, and this constancy of boiling point is obtained sooner if the temperature of the oil bath is regulated to a constant temperature before distillation is started. No more than 50 cc. (of which approximately 10 cc. is water) should come over in the first fraction. If the temperature of the bath is regulated carefully, practically all the product will distil at a constant temperature.
5. The product is dissolved by gentle heating and the solution is then cooled to 0° or below for several hours. The material remaining in the mother liquor (about 30 per cent of the total) may be recovered as impure, oily oxime by evaporation of the alcohol.
6. The melting point given was determined by the capillary-tube method and depended on the rate of heating. The melting point as given in the literature varies from 50° to 58°.

7. [Cyclohexanone oxime](#) can be prepared in the same percentage yields by a procedure which differs from the above only in that the reaction mixture becomes solid before the addition of the [sodium carbonate](#) is complete. After all the [sodium carbonate](#) has been added, steam is passed in until the oxime is melted, and the mixture is shaken vigorously for fifteen minutes at five-minute intervals. [Cyclohexanone oxime](#) boils at 100–105°/10–12 mm. and melts at 87–88°.

### 3. Discussion

Heptaldoxime has been prepared only by the action of the aldehyde on an aqueous solution of [hydroxylamine hydrochloride](#) in the presence of alkali;<sup>1</sup> the method described above is a modification of that given by Westenberger.<sup>1</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 76](#)
- [Org. Syn. Coll. Vol. 2, 318](#)
- [Org. Syn. Coll. Vol. 2, 371](#)
- [Org. Syn. Coll. Vol. 8, 568](#)

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### References and Notes

1. Westenberger, *Ber.* **16**, 2992 (1883); Goldschmidt and Zanolli, *ibid.* **25**, 2593 (1892); Bourgeois and Dambmann, *ibid.* **26**, 2860 (1893).

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### Appendix

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

Heptaldoxime

[ethyl alcohol](#) (64-17-5)

[sodium carbonate](#) (497-19-8)

[Hydroxylamine hydrochloride](#) (5470-11-1)

[Cyclohexanone oxime](#) (100-64-1)

[Enanthaldehyde oxime](#) (629-31-2)

[heptanonitrile](#) (629-08-3)

[heptaldehyde](#) (111-71-7)

[n-heptylamine](#) (111-68-2)