



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.

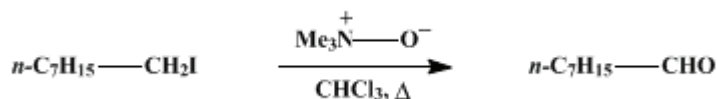
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures 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. 5, p.872 (1973); Vol. 47, p.96 (1967).*

## OCTANAL



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Checked by Claibourne Smith and V. Boekelheide.

### 1. Procedure

To a solution of 30 g. (0.4 mole) of anhydrous trimethylamine oxide (Note 1) in 100 ml. of dry chloroform placed in a 250-ml. three-necked, round-bottomed flask fitted with a reflux condenser, a stirrer, and a dropping funnel with protection against moisture is added 48.0 g. (0.2 mole) of *n*-octyl iodide (Note 2) dropwise with stirring. At the beginning of the addition the flask is warmed to 40–50° on a steam bath to initiate the reaction. The start of the reaction can be recognized by the evolution of heat, and the rate of addition can then be adjusted to maintain the temperature around 50°. Overall the addition requires about 20–30 minutes. When addition is complete, the solution is boiled under reflux for another 20 minutes. Then the solution is cooled, and 110 ml. of 2*N* aqueous sulfuric acid solution is added with stirring. The chloroform layer is separated and washed successively with water, 2*N* aqueous sodium carbonate solution, and again with water. After the chloroform solution has been dried over sodium sulfate, it is concentrated under reduced pressure, and then the residue is distilled. The first distillation (Note 3) is carried out at atmospheric pressure and gives 12.0–12.5 g. of a crude oil, b.p. 155–165°. Redistillation using a simple Vigreux column gives 10.6–11.0 g. (41.5–43%) of a colorless oil, b.p. 69–71° (19 mm.), *n*<sup>20</sup><sub>D</sub> 1.4167.

### 2. Notes

1. Trimethylamine oxide is normally available as a hydrate, and for the present preparation it is necessary to convert it to its anhydrous form. A convenient way of doing this is as follows. A solution of 45.0 g. of trimethylamine oxide dihydrate (supplied by Beacon Chemicals) is dissolved in 300 ml. of warm dimethyl-formamide and placed in a three-necked flask set up for distillation. At atmospheric pressure the flask is heated and solvent distilled off until the boiling point reaches 152–153°. Then the pressure is reduced using a water aspirator, and the remainder of the solvent is distilled. At the end of the distillation the temperature of the bath is slowly raised to 120°. The residual anhydrous trimethylamine oxide (30 g.) can be dissolved in 100 ml. of chloroform and may remain in the same flask for use in the present preparation.
2. In place of *n*-octyl iodide other derivatives such as *n*-octyl bromide, *n*-octyl *p*-toluenesulfonate, and *n*-octyl chlorosulfonate can be substituted; the submitter reports that the yields of octanal in these cases are comparable.
3. At this stage the product is a waxy semisolid, presumably a trimer or polymer of octanal, and the higher temperature of an atmospheric distillation is needed to generate the monomeric octanal.

### 3. Discussion

Octanal has been prepared by the reduction of caprylonitrile with hydrogen chloride and stannous chloride,<sup>2</sup> by the passage of a mixture of caprylic acid and formic acid over titanium dioxide<sup>3</sup> or manganous oxide,<sup>4</sup> by dehydrogenation of 1-octanol over copper,<sup>5</sup> and by oxidation of 1-octanol.<sup>6</sup>

### 4. Merits of the Preparation

The conversion of alkyl halides to aldehydes is a synthetic step of broad utility. Earlier procedures for such conversions involving the use of dimethyl sulfoxide<sup>7</sup> or pyridine *N*-oxide<sup>8</sup> have worked best with activated alkyl halides, although Kornblum has described a modification of the dimethyl sulfoxide procedure for use with ordinary aliphatic halides.<sup>9</sup> The present procedure using trimethylamine oxide

avoids some of the complicating side reactions of [pyridine N-oxide](#) and is useful with ordinary aliphatic halides.<sup>10,11</sup>

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## References and Notes

1. Max-Planck Institute for Medical Research, Heidelberg, Germany.
  2. H. Stephen, *J. Chem. Soc.*, **127**, 1875 (1925).
  3. P. Sabatier and A. Maihle, *Compt. Rend.*, **154**, 561 (1912).
  4. P. Sabatier and A. Maihle, *Compt. Rend.*, **158**, 985 (1914).
  5. R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 56 (1911).
  6. R. P. A. Sneed and R. B. Turner, *J. Am. Chem. Soc.*, **77**, 190 (1955).
  7. N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).
  8. W. Feely, W. L. Lehn, and V. Boekelheide, *J. Org. Chem.*, **22**, 1135 (1957).
  9. N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).
  10. V. Franzen and S. Otto, *Ber.*, **94**, 1360 (1961).
  11. L. D. Bergelson and M. M. Shemyakin, *Angew. Chem. Intern. Ed. Engl.*, **3**, 250 (1964).
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## Appendix

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

[sulfuric acid](#) (7664-93-9)

[hydrogen chloride](#) (7647-01-0)

[chloroform](#) (67-66-3)

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

[n-octyl bromide](#) (111-83-1)

[sodium sulfate](#) (7757-82-6)

[formic acid](#) (64-18-6)

[stannous chloride](#)

[copper](#) (7440-50-8)

[1-Octanol](#) (111-87-5)

[caprylic acid](#) (124-07-2)

[n-octyl iodide](#) (629-27-6)

[manganous oxide](#)

[titanium dioxide](#)

dimethyl-formamide (68-12-2)

dimethyl sulfoxide (67-68-5)

Pyridine N-oxide (694-59-7)

OCTANAL (124-13-0)

trimethylamine oxide (1184-78-7)

trimethylamine oxide dihydrate (62637-93-8)

caprylonitrile (124-12-9)

n-octyl p-toluenesulfonate (3386-35-4)

n-octyl chlorosulfonate