



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.

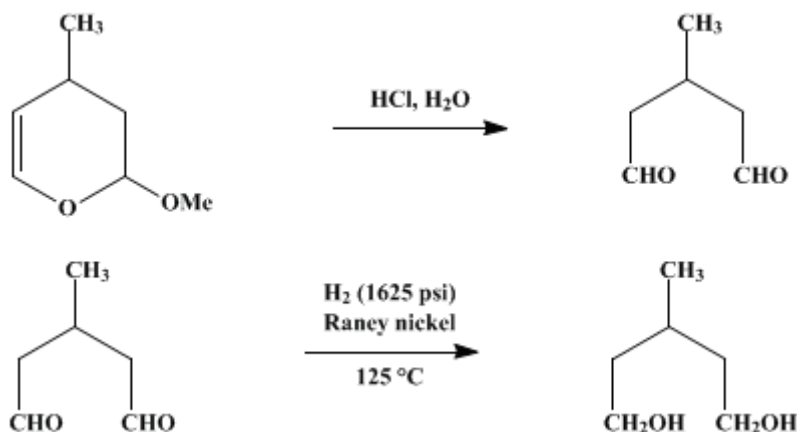
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.660 (1963); Vol. 34, p.71 (1954).

3-METHYL-1,5-PENTANEDIOL

[1,5-Pentanediol, 3-methyl-]



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Checked by T. L. Cairns and John F. Harris, Jr..

1. Procedure

In a 2-l. three-necked flask equipped with a stirrer and thermometer are placed 336 g. (2.62 moles) of 3,4-dihydro-2-methoxy-4-methyl-2H-pyran (p. 311), 630 ml. of water, and 24 ml. of concentrated hydrochloric acid (sp. gr. 1.19). The mixture is stirred for 2 hours, during which the temperature may reach 50° but should not be permitted to rise higher. Solid sodium bicarbonate is then added until the solution is neutral to pH indicator paper (Note 1). The entire reaction mixture weighing about 1 kg. together with 39 g. of Raney nickel² is introduced into a 3-l. stainless-steel rocking hydrogenation autoclave. A hydrogen pressure of at least 1625 p.s.i. (Note 2) is applied, and the autoclave is heated to 125° and held there with shaking for 4 hours. The mixture is allowed to cool overnight, and the catalyst is separated either by suction filtration through Filter-Cel or by centrifugation. The solution is distilled through a 12-in. Vigreux column. After the methanol and water are separated, the 3-methyl-1,5-pentanediol distils at 139–146°/17 mm., 149–150°/25 mm. The yield is 251–256 g. (81–83%), n_D^{25} 1.4512–1.4521.

2. Notes

1. The submitters report that β -methylglutaraldehyde may be isolated at this point from an analogous hydrolysis. The hydrolysis is carried out with 196 g. of 3,4-dihydro-2-methoxy-4-methyl-2H-pyran in 650 ml. of water and 15 ml. of concentrated hydrochloric acid for 3 hours. After neutralization with sodium bicarbonate, the solution is saturated with sodium chloride and extracted continuously with ether for 20 hours. The ether is removed by distillation, and the product is dried thoroughly by azeotropic distillation using a benzene-hexane mixture. Distillation affords β -methylglutaraldehyde, b.p. 85–86°/15 mm., n_D^{25} 1.4307–1.4351. Yields up to 90% have been secured. The aldehyde polymerizes on standing but is stable as a 50% solution in water or ether. The monomer may be recovered by careful destructive distillation of the polymer.

2. The initial hydrogen pressure should be high enough that it does not fall below 1000 p.s.i. during the shaking period.

3. Discussion

3-Methyl-1,5-pentanediol has been prepared by the hydrogenation of ethyl β -methylglutarate;³ by the hydrogenation of ethyl β -methyl- α,γ -dicarbethoxyglutarate;⁴ by the hydrogenation of β -

methylglutaraldehyde;⁵ and by heating 3,4-dihydro-2-methoxy- 4-methyl-2H-pyran with water, hydrogen, and copper-chromium oxide, nickel on kieselguhr,⁵ or Raney nickel catalyst.⁶

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 677

References and Notes

1. Central Research Department, Monsanto Chemical Company, Dayton 7, Ohio.
 2. *Org. Syntheses Coll. Vol. 3*, 181 (1955).
 3. Paden and Adkins, *J. Am. Chem. Soc.*, **58**, 2487 (1936).
 4. Wojcik and Adkins, *J. Am. Chem. Soc.*, **55**, 4939 (1933).
 5. Longley, Emerson, and Shafer, *J. Am. Chem. Soc.*, **74**, 2012 (1952); Ashley, Collins, Davis, and Sirett, *J. Chem. Soc.*, **1958**, 3298.
 6. Smith, U. S. pat. 2,546,019 [*C. A.*, **45**, 7589 (1951)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

3,4-dihydro-2-methoxy- 4-methyl-2H-pyran

hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

nickel,
Raney nickel (7440-02-0)

Copper-Chromium Oxide

benzene-hexane (1077-16-3)

3,4-Dihydro-2-methoxy-4-methyl-2H-pyran (53608-95-0)

3-Methyl-1,5-pentanediol,
1,5-Pentanediol, 3-methyl- (4457-71-0)

β -Methylglutaraldehyde (6280-15-5)

ethyl β -methylglutarate

ethyl β -methyl- α,γ -dicarboxylate

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