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.

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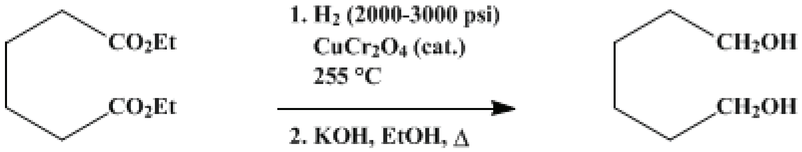
Organic Syntheses, Coll. Vol. 2, p.325 (1943); Vol. 19, p.48 (1939).

HEXAMETHYLENE GLYCOL

[1,6-Hexanediol]



Submitted by W. A. Lazier, J. W. Hill, and W. J. Amend.
Checked by R. L. Shriner and J. F. Kaplan.

1. Procedure

In a steel reaction vessel (Note 1), capable of withstanding high pressures with an adequate safety factor (Note 2) and having a capacity of 400 cc. or more, are placed 252 g. (1.25 moles) of ethyl adipate (b.p. 144–145°/29 mm.) (p. 264) and 20 g. of copper chromite catalyst, prepared either with or without the addition of barium (p. 142). The reaction vessel is closed, made gas tight, and secured in a suitable agitating device. After connection is made with the hydrogen supply, hydrogen is introduced until a pressure of 2000 to 3000 lb. per sq. in. is reached (Note 2).

Agitation is started, and the reaction system is heated as rapidly as possible to 255°. The temperature is maintained at 255° (Note 3), and hydrogenation is continued until hydrogen absorption is complete (Note 4). The agitation is now stopped, the vessel cooled, and the pressure released. With the aid of four 25-cc. portions of 95 per cent alcohol the reaction mixture is transferred to a 600-cc. beaker. The catalyst is removed by filtering or centrifuging, and is washed with four more 25-cc. portions of alcohol (Note 5). To the reaction product (Note 6), 50 cc. of 40 per cent sodium hydroxide solution is added, and the alcoholic solution is boiled for two hours under a reflux condenser. The mixture is transferred to a 1-l. distilling flask and the alcohol removed by distilling to a vapor temperature of 95°. The hot residue is transferred to an apparatus for the continuous extraction of liquids (p. 615), using 50 cc. of water to rinse the flask, and the solution is exhaustively extracted with ether (Note 7). The ether is distilled, and, after the removal of water and alcohol, the glycol is distilled under reduced pressure in a 250-cc. Claisen flask. The yield is 125–132 g. (85–90 per cent of the theoretical amount). Hexamethylene glycol boils at 143–144° (bath at 160°) under 4 mm. pressure and melts at 41–42°.

2. Notes

1. Suitable reaction vessels and apparatus for agitation of the reaction mixture are commercially available[1], [2] or may be constructed.[3]
2. The pressure of hydrogen to be used is dependent upon the equipment available. Hydrogen in commercial cylinders is sold at a maximum pressure of 2000 lb. per sq. in. Special equipment for compressing hydrogen may be purchased at a reasonable price.[1] The original pressure of hydrogen should not be more than 2000 lb. if the maximum working pressure of the equipment for hydrogenation is 5000 lb. If the working pressure is 10,000 lb. the original pressure in the reaction vessel may be as much as 3000 lb. The full operating pressure is not applied in the beginning since the pressure will rise as the reaction vessel is heated; thus, at 255° the pressure will be 1.8 times as high as it was at 20°. The pressure drops as hydrogenation proceeds; the progress of the reaction may be followed by the change in pressure readings, and completion of the reaction is indicated by the constancy of the pressure readings.
3. The temperature is controlled preferably by an automatic controller operating through a relay which periodically cuts off the supply of electric current.
4. The time (six to twelve hours) required to complete the reaction is a function of the pressure of the hydrogen, activity of the catalyst, and purity of the ethyl adipate. Unless a high pressure of hydrogen is used originally or the reaction vessel is of large capacity (2 l.) it will be necessary to introduce more

hydrogen into the reaction vessel; the pressure should never be less than 1500 lb. per sq. in. if the reaction is to run smoothly to completion.

5. The catalyst is most readily removed by centrifuging. If this is not convenient, it may be collected on a sintered glass filter or Büchner funnel.

6. At this point, the amount of ester present may be determined by obtaining the saponification value of the weighed mixture. This procedure is especially desirable when the condition of the apparatus with respect to the possible presence of poisons is unknown, or a new preparation of catalyst is being used. After a batch of catalyst has been tested and the apparatus calibrated so that essentially complete reduction is assured, it is possible to isolate the glycol by fractional distillation at this stage.

According to Burks, Jr., and Adkins [private communication and J. Am. Chem. Soc. **62**, 3300 (1940)] the hydrogenation is reversible and the reaction product always contains esters. In order to obtain hexamethylene glycol free of esters a simpler procedure than that given above is recommended: Thirty grams of crude glycol is dissolved in 50 cc. of water and extracted with four 50-cc. portions of benzene. The water solution is distilled through a modified Widmer column. The recovery of glycol, free of ester, is 93 per cent.

7. The time required for complete extraction varies from twenty-four to fifty hours. It depends on the design of the apparatus and the rate of distillation of the ether. The extraction can be followed by observing the decrease in volume of the aqueous layer containing the glycol. The extraction is complete when the evaporation of a small amount of the supernatant ether on a watch glass leaves no residue. Benzene may be substituted for ether in the extraction.

3. Discussion

Hexamethylene glycol has been prepared by treating hexamethylene iodide with silver acetate and hydrolyzing the acetate,[4] by hydrolyzing the bromide,[5] by reducing ethyl adipate with sodium and alcohol,[6] and by the method here described.[7] The catalytic hydrogenation over copper-chromium oxide of the carbethoxy group to the carbinol group is a very useful and general method for the preparation of mono- and dihydric alcohols.[3], [8]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 154
- Org. Syn. Coll. Vol. 3, 446
- Org. Syn. Coll. Vol. 4, 323

References and Notes

1. American Instrument Company, Silver Spring, Maryland.
2. Parr Instrument Company, Moline, Illinois.
3. Adkins, Ind. Eng. Chem., Anal. Ed. **4**, 342 (1932); "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," pp. 29–39, University of Wisconsin Press, Madison, Wisconsin, 1937.
4. Hamonet, Bull. soc. chim. (3) **33**, 538 (1905).
5. Haworth and Perkin, J. Chem. Soc. **65**, 598 (1894).
6. Bouveault and Blanc, Compt. rend. **137**, 328 (1903); Bull. soc. chim. (3) **31**, 1203 (1904).
7. Lazier, U. S. pat. 2,079,414 [C. A. **31**, 4340 (1937)]; U. S. pat. 2,137,407 [C. A. **33**, 1758 (1939)].
8. Adkins and Folkers, J. Am. Chem. Soc. **53**, 1095 (1931); **54**, 1145 (1932); Wojcik and Adkins, ibid. **55**, 4939 (1933).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

sodium and alcohol

alcohol (64-17-5)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

Ethyl adipate (626-86-8)

barium (7440-39-3)

COPPER CHROMITE

Copper-Chromium Oxide

Hexamethylene glycol,
1,6-Hexanediol (629-11-8)

hexamethylene iodide (629-09-4)

silver acetate (563-63-3)