



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.

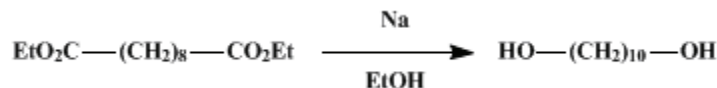
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.154 (1943); Vol. 14, p.20 (1934).

DECAMETHYLENE GLYCOL

[1,10-Decanediol]



Submitted by R. H. Manske

Checked by W. H. Carothers and W. L. McEwen.

1. Procedure

To a solution of 65 g. (0.25 mole) of [ethyl sebacate](#) (p. 277) in 800 cc. of absolute [ethyl alcohol](#) (Note 1) contained in a 3-l. round-bottomed flask, to which is attached a 60-cm. bulbed reflux condenser protected by a calcium chloride drying tube, is added 70 g. (3 gram atoms) of [sodium](#) in large pieces in one lot. The somewhat vigorous reaction is easily kept under control by immersing the entire flask in a mixture of crushed ice and water. In a short time the reaction has subsided somewhat; the flask is then removed from the cooling mixture, and the reaction is allowed to proceed without external cooling. Reduction is completed by heating the mixture on a steam bath until all the [sodium](#) has dissolved. The partly cooled mixture is diluted with 300 cc. of water and heated on the steam bath until no more alcohol distils. The remaining small amount of alcohol is removed by gently applying suction from a water pump. The residue is diluted with about 600 cc. of hot water, and the mixture is allowed to cool without being disturbed. The separated oil solidifies to a solid cake from which the lower aqueous layer is easily decanted. The solid is washed once with a little cold water, drained as completely as possible, and dried by heating in the flask on a steam bath under reduced pressure. The residue is extracted with four successive 250-cc. portions of hot [benzene](#). The united extract is clarified with a little charcoal, filtered, and concentrated to a volume of about 60 cc. About 200 cc. of [alcohol](#) is added; the solution is filtered, concentrated to about 60 cc., and mixed with an equal volume of hot [benzene](#). On slow cooling the mixture sets to a solid mass of large crystals, which are filtered and washed with [ether](#). The yield of this product, which melts at 72–74° (corr.), is 32–33 g. (73–75 per cent of the theoretical amount) (Note 2), (Note 3), and (Note 4).

2. Notes

1. The alcohol must be perfectly dry, for any water present will cause immediate saponification of the ester with a consequent loss of yield. An excellent method for preparing completely anhydrous alcohol from [alcohol](#) of 99.5 per cent strength consists in dissolving 7 g. of [sodium](#) in 1 l. of the [alcohol](#), adding 27.5 g. of a high-boiling ester such as [ethyl phthalate](#), refluxing, and distilling.¹
2. When several runs of the size indicated above or a single large run is made, the combined mother liquors may be evaporated free of solvent and the residue distilled under reduced pressure. The distillate on recrystallization from alcohol-benzene yields, however, only 5 to 7 grams of pure glycol per mole of sebacic ester.
3. The general method of Bouveault and Blanc has been used extensively for the preparation of glycols. Various modifications of detail have been suggested. Most of them are probably trivial or immaterial. In the experience of the checkers the rapid addition of the alcohol-ester mixture to the [sodium](#) gives results approximately equal to those described above, but mechanical stirring of the reaction mixture seriously reduces the yield.² The method used for isolating the glycol must be adapted to the properties of the glycol. At least for small runs the method of crystallization described here is the most suitable for [decamethylene glycol](#). Lower members of the series are less readily crystallized. C. S. Marvel in a private communication has pointed out that for these glycols continuous [ether](#) extraction is the best method, and this has been used for [hexamethylene glycol](#) with success by the checkers. Using the procedure described the checkers have prepared the following glycols.

Yield, Per Cent

Heptamethylene glycol	b.p. 143–146°/8 mm.	88
Nonamethylene glycol	b.p. 147–150°/2 mm.	71
Undecamethylene glycol	m.p. 48–50°	57
Tridecamethylene glycol	m.p. 75–77°	88
Tetradecamethylene glycol	m.p. 83–85°	61
Octadecamethylene glycol	m.p. 96–98°	54

The **heptamethylene glycol** was separated by continuous **ether** extraction from the alkaline reduction solution after the latter had been diluted and distilled to remove the alcohol. The **nonamethylene glycol** was separated from the alkaline liquor by decantation (as above) and distilled. All the others were crystallized from **benzene** (without alcohol). Equally successful results have also been obtained with larger runs (e.g., 0.5 mole of ester).

4. **Decamethylene glycol** can also be prepared in excellent yields by the reduction of commercial **butyl sebacate** according to the procedure given for **hexamethylene glycol** on p. 325.

3. Discussion

Decamethylene glycol is best prepared by the reduction of sebacic esters either with **sodium** and an alcohol,² the Bouveault-Blanc procedure described above, or with **hydrogen** and a catalyst³—a procedure for which directions are given on p. 325. Both methods are applicable to the preparation of many other glycols.

Decamethylene glycol has also been prepared by the reduction of **sebacamide** with **sodium** and **amyl alcohol**⁴ and by the reduction of **methyl sebacate** with **sodium** and liquid **ammonia** in absolute **alcohol**.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 262
- Org. Syn. Coll. Vol. 3, 397
- Org. Syn. Coll. Vol. 3, 637
- Org. Syn. Coll. Vol. 3, 829
- Org. Syn. Coll. Vol. 4, 427
- Org. Syn. Coll. Vol. 4, 461
- Org. Syn. Coll. Vol. 4, 630
- Org. Syn. Coll. Vol. 5, 1031

References and Notes

1. Smith, J. Chem. Soc. **1927**, 1288; Manske, J. Am. Chem. Soc. **53**, 1106 (1931).
 2. Bouveault and Blanc, Compt. rend. **137**, 329 (1903); Bull. soc. chim. (3) **31**, 1205 (1904); Ger. pat. 164, 294 [Fr. **8**, 1260 (1905–7)]; Franke and Kienberger, Monatsh. **33**, 1191 (1912); Chuit, Helv. Chim. Acta **9**, 264 (1926); Carothers, Hill, Kirby, and Jacobson, J. Am. Chem. Soc. **52**, 5287 (1930).
 3. Folkers and Adkins, *ibid.* **54**, 1146 (1932).
 4. Scheuble, Monatsh. **24**, 623 (1903); Scheuble and Loebler, *ibid.* **25**, 344 (1904); Alberti and Smieciuszewski, *ibid.* **27**, 411 (1906).
 5. Chablay, Compt. rend. **156**, 1021 (1913); Ann. chim. (9) **8**, 216 (1917).
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Appendix

Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

alcohol-benzene

ethyl alcohol,
alcohol (64-17-5)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium (13966-32-0)

amyl alcohol (71-41-0)

Decamethylene glycol,
1,10-Decanediol (112-47-0)

Ethyl sebacate (693-55-0)

ethyl phthalate

Hexamethylene glycol (629-11-8)

Heptamethylene glycol (629-30-1)

Nonamethylene glycol (3937-56-2)

Undecamethylene glycol (765-04-8)

Tridecamethylene glycol

Tetradecamethylene glycol (19812-64-7)

Octadecamethylene glycol

butyl sebacate

sebacamide (1740-54-1)

methyl sebacate (818-88-2)