Organic Syntheses

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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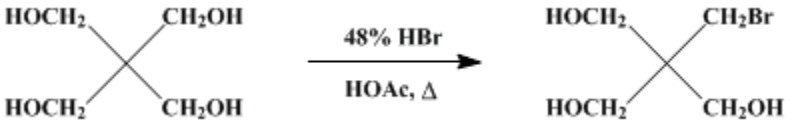
MONOBROMOPENTAERYTHRITOL

[1,3-Propanediol, 2-(bromomethyl)-2-(hydroxymethyl)-]



Submitted by S. Wawzonek, A. Matar, and C. H. Issidorides[1].
Checked by Charles C. Price and G. Venkat Rao.

1. Procedure

In a 3-l. two-necked flask (Note 1) fitted with a dropping funnel and a reflux condenser are placed 200 g. (1.47 moles) of pentaerythritol, 1.5 l. of glacial acetic acid, and 17 ml. of 48% hydrobromic acid (Note 2). After a reflux period of 1.5 hours, 170 ml. of 48% hydrobromic acid is added and the solution is heated under reflux for an additional 3 hours. At the end of this time 96 ml. of 48% hydrobromic acid is added and the heating under reflux is continued for 3 hours. The solution is distilled under reduced pressure to remove as much of the acetic acid and the water as possible, first on a steam bath and finally for 15 minutes in an oil bath at 140–150°, as the pressure is reduced to 10 mm. The viscous residue is transferred to a 2-l. flask and treated with 750 ml. of 98% ethanol and 50 ml. of 48% hydrobromic acid. The flask is provided with an efficient fractionating column (Note 3), and the solution is fractionated slowly until about 500 ml. of distillate is collected. Then a second 750-ml. portion of ethanol is added, and the fractionation is continued slowly until 750 ml. more distillate is collected (Note 4). Finally, the flask is fitted with a Claisen head and a condenser set for downward distillation, and the remaining alcohol is removed as completely as possible under reduced pressure.

Benzene (500 ml.) is added to the residue and distilled at atmospheric pressure. The last traces of benzene are removed by heating for 15 minutes in an oil bath at 150°, as the pressure is reduced to 8 mm. The same procedure is repeated, using a second 500-ml. portion of benzene (Note 5). The viscous residue is then heated under reflux for several hours with 500 ml. of dry ether, with frequent shaking, until it becomes white and granular (Note 6). After cooling thoroughly, the ether is decanted, and the solid is washed twice with two 200-ml. portions of dry ether. The solid is powdered thoroughly and dried in a vacuum desiccator. The dry solid is then extracted exhaustively in a Soxhlet extractor with 600 ml. of dry ether (Note 7). The ether extract is cooled overnight in an ice bath, and the precipitated monobromopentaerythritol is collected by filtration and washed with two 200-ml. portions of cold, dry ether. The yield of crude product melting at 72–73° is 145–160 g. (49–54% of the theoretical). One recrystallization from a mixture of 3 parts of chloroform and 2 parts of ethyl acetate by volume raises the melting point to 75–76°, recovery 75–85%.

2. Notes

1. For best results the flask should have standard-taper, ground-glass fittings.
2. Eastman Kodak Company white label grade pentaerythritol and 48% hydrobromic acid were used.
3. A 40-cm. column packed with glass beads is satisfactory.
4. The fractionation should be carried out slowly to ensure complete alcoholysis of the bromoacetate. The boiling point during the collection of the first 500 ml. of distillate remains constant at around 72°, corresponding to the ethanol-ethyl acetate azeotrope.
5. The purpose of this operation is to remove completely the water present in the product. Toluene may be substituted for benzene.
6. If the product has a tendency to form a hard mass, it is advisable to break up the solid with a stirring rod.
7. The extraction is very slow and requires several hours for completion, depending upon the rate of refluxing of the ether. Usually crystals of the monobromopentaerythritol begin to deposit on the walls of

the extraction flask after the first hour. At the end of the extraction 30–35 g. of unchanged pentaerythritol remains in the extraction thimble. Dibromopentaerythritol, formed as a side product, is present in the ether washings.

3. Discussion

Monobromopentaerythritol has been prepared by the action of 66% hydrobromic acid on pentaerythritol in glacial acetic acid[2] and by the action of 66% hydrobromic acid on pentaerythritol[3] at 120°. The procedure described is a modification of the method of Beyaert and Hansens.[3]

References and Notes

1. State University of Iowa, Iowa City, Iowa.
2. Beyaert and Hansens, *Natuurw. Tijdschr. (Ghent)*, **22**, 249 (1940) [*C. A.*, **37**, 5373 (1943)].
3. Barbiere and Matti, *Bull. soc. chim. France* [5]**5**, 1565 (1938).

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

ethanol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

ethyl acetate (141-78-6)

ether (60-29-7)

chloroform (67-66-3)

HYDROBROMIC ACID (10035-10-6)

toluene (108-88-3)

Pentaerythritol (115-77-5)

Monobromopentaerythritol

1,3-Propanediol, 2-(bromomethyl)-2-(hydroxymethyl)- (19184-65-7)

Dibromopentaerythritol