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.

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.

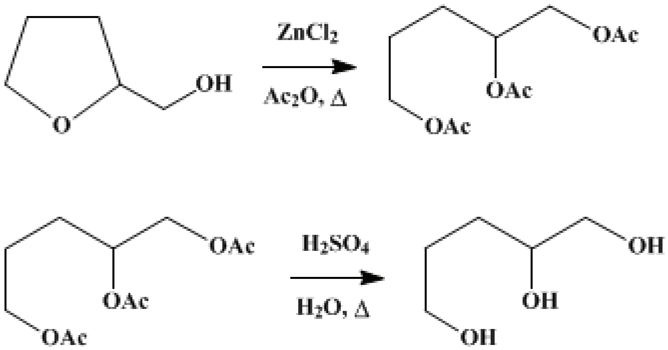
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.029.0089

Organic Syntheses, Coll. Vol. 3, p.833 (1955); Vol. 29, p.89 (1949).

1,2,5-TRIHYDROXYPENTANE

[1,2,5-Pentanetriol]



Submitted by Oliver Grummitt, James A. Stearns, and A. A. Arters.
Checked by Eugene Dineen, Christopher L. Wilson, and Charles C. Price.

1. Procedure

In a 5-l. three-necked flask fitted with a mercury-sealed mechanical stirrer, a 500-ml. dropping funnel, and an efficient reflux condenser are placed 2630 ml. (2856 g., 28 moles) of acetic anhydride and 57 g. of crushed anhydrous zinc chloride. This mixture is stirred and brought to gentle boiling. After 5–10 minutes at reflux, 680 ml. (714 g., 7 moles) of redistilled tetrahydrofurfuryl alcohol (Note 1) is added from the dropping funnel at such a rate that the mixture refluxes vigorously. This addition requires about 30 minutes. The mixture is then stirred and refluxed gently for 24 hours. After being cooled, about one-half of the liquid is decanted from the zinc chloride residue through a glass wool plug in a funnel into a 2-l. Claisen flask and then distilled under reduced pressure. The second portion is likewise distilled. The total weight of fore-run is 1740–1780 g. (Note 2). The 1,2,5-triacetoxypentane is collected at 155–165°/14 mm. The yield is 1500–1550 g. (87–90%).

Fifteen hundred grams (6.1 moles) of the ester and 1.2 l. of 1% sulfuric acid (6.9 ml. of concentrated acid in 1.2 l. of solution) are added to a 5-l. round-bottomed flask fitted with a reflux condenser. The mixture is heated strongly and agitated by tilting the ring stand back and forth until the two layers become homogeneous. This initial hydrolysis step requires 15–30 minutes. When homegenity is attained, the flask and condenser are set for steam distillation. The flask is heated by a Meker burner to maintain approximately constant volume, and the mixture is vigorously steam-distilled until 20 l. of distillate has been collected (Note 3). The residue is allowed to cool and then made basic to litmus paper by the addition of 10–20 g. of lime in small portions with vigorous agitation. The calcium sulfate is removed by suction filtration, the filtrate tested again with litmus paper to make certain that it is basic (Note 4), and the filtrate distilled under reduced pressure. This is most conveniently done by placing about one-half of the solution in a 2-l. Claisen flask, heating the flask in an oil bath at 100–110°, and distilling the water under the pressure of the water pump. The remainder of the filtrate is added, the water is removed, and the distillation is continued with an oil or mercury-vapor pump. The yield of 1,2,5-trihydroxypentane collected at 167–170°/0.5–1.0 mm. is 460–520 g. (63–71%); n_{D}^{25} 1.4730 (Note 5).

2. Notes

1. Tetrahydrofurfuryl alcohol from the Quaker Oats Company was redistilled, and the portion boiling at 175–177° was used. If the 1001 industrial grade of alcohol is used without purification, the yield of triacetate is about 70% of the theoretical.
2. This consists mostly of acetic acid, acetic anhydride, and some tetrahydrofurfuryl acetate. By fractional distillation through a 15-in. glass-helix-packed column, ½ in. in diameter, about 700 g. of

acetic acid boiling at 117–125° and about 1075 g. of acetic anhydride boiling at 137–142° can be recovered.

3. With 10-mm. glass tubing for the steam inlet and outlet and an efficient condenser the maximum rate of steam distillation is 3 l. per hour. The 20 l. of distillate collected contains 95% of the calculated yield of acetic acid. The removal of the acetic acid is slow because the rate of hydrolysis in the final stages appears to be slow and the rate of acetic acid distillation is slow. The remainder of the acid is collected so slowly that it is not considered worth while to distil further, although the yield of product can be slightly increased.

4. If an acidic solution is distilled, the yield of product is decreased, probably because of dehydration and etherification reactions.

5. Analysis of this product for hydroxyl group content by the acetic anhydride-pyridine method gave 40.0%, compared to a calculated value of 42.5%, indicating a purity of 94%.

3. Discussion

1.2.5-Trihydroxypentane has been made by saponification of 1,2,5-triacetoxypentane with barium hydroxide[1,2] and by hydrolysis with 0.1 *N* hydrochloric acid.[3] The triacetoxypentane has been made by the action of potassium acetate and acetic anhydride on 4,5-dibromopentanol-1[1] or 1,2,5-tribromopentane[2,4] or 1-chloro-4,5-diacetoxypentane,[5] but it is most conveniently made by the reaction of acetic anhydride with tetrahydrofurfuryl alcohol.[3,4] The present method is a modification of that described by Wilson.[3]

References and Notes

1. Paul, *Compt. rend.*, **192**, 1574 (1931).
2. Paul, *Ann. chim.*, (10) **18**, 303 (1932).
3. Wilson, *J. Chem. Soc.*, **1945**, 48.
4. Paul, *Bull. soc. chim. France*, **53**, 417 (1933).
5. Paul, *Compt. rend.*, **211**, 645 (1940).

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

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

calcium sulfate (7778-18-9)

zinc chloride (7646-85-7)

barium hydroxide (17194-00-2)

tetrahydrofurfuryl alcohol (97-99-4)

potassium acetate (127-08-2)

4,5-dibromopentanol-1

1,2,5-Trihydroxypentane,
1,2,5-Pentanetriol,
1.2.5-Trihydroxypentane (14697-46-2)

1,2,5-Triacetoxypentane (5470-86-0)

tetrahydrofurfuryl acetate (637-64-9)

triacetoxypentane

1,2,5-tribromopentane

1-chloro-4,5-diacetoxypentane