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.

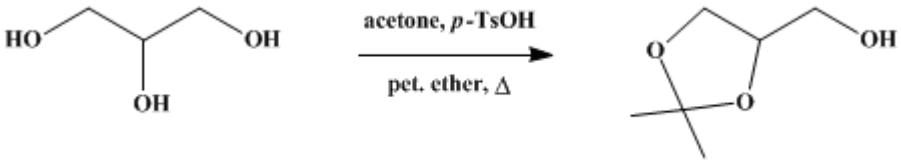
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI: 10.15227/orgsyn.028.0073

Organic Syntheses, Coll. Vol. 3, p.502 (1955); Vol. 28, p.73 (1948).

dl-ISOPROPYLIDENEGLYCEROL

[Glycerol, isopropylidene-; also 1,3-dioxolane-4-methanol, 2,2-dimethyl-]



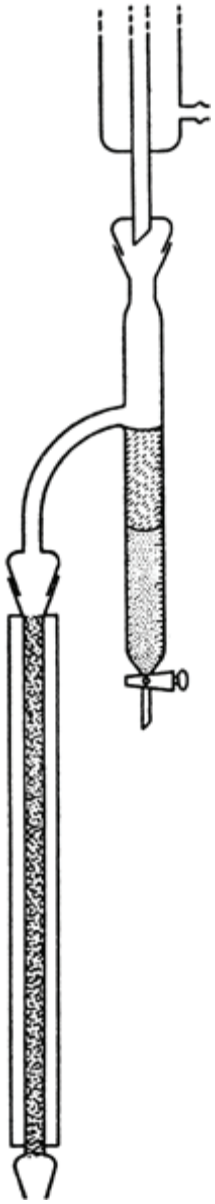
Submitted by Mary Renoll and Melvin S. Newman.
Checked by R. L. Shriner and Arne Langsjoen.

1. Procedure

In a 1-l. three-necked flask, fitted with a sealed mechanical stirrer and a fractionating column (about 2 by 45 cm., packed with glass helices) attached to a total reflux phase-separating head (Fig. 15) (Note 1), are placed 237 g. (300 ml., 4.09 moles) of acetone (Note 2), 100 g. (1.09 moles) of glycerol (Note 3), 300 ml. of low-boiling petroleum ether (Note 4), and 3.0 g. of *p*-toluenesulfonic acid monohydrate. The third neck is closed with a cork or a ground-glass stopper, and the mixture is heated (Note 5) with stirring so that the petroleum ether refluxes as rapidly as the column permits. The stirring and refluxing are continued until no more water collects in the trap of the separating head; the time required varies between 21 and 36 hours (Note 6).

The mixture is cooled to room temperature, and 3.0 g. of powdered, freshly fused sodium acetate is added. Stirring is continued for 30 minutes; the mixture is then filtered, and the petroleum ether and excess acetone are removed by distillation under reduced pressure (water pump). The residual liquid is distilled from a modified Claisen flask. The fraction boiling at 80–81°/11 mm. is collected. The yield of colorless isopropylideneglycerol (n_D^{25} 1.4339, d_4^{25} 1.062) is 125–129 g. (87–90%).

Fig. 15.



2. Notes

1. During operation, the apparatus shown in Fig. 15 requires no attention beyond occasional draining of the water trap. It is suitable for a number of preparations in which water is removed by distillation with an immiscible solvent; it functions only when the condensate separates into two phases, of which water is the more dense.
2. The acetone was the 99.5% grade obtained from the Carbide and Carbon Chemicals Company.
3. The glycerol should be of U.S.P. grade; if it has absorbed moisture, it may be dehydrated by heating at 170° in an open dish under a hood for 3 hours.[1]
4. Skellysolve F, b.p. 35–55°, obtainable from the Skelly Oil Company, is suitable.
5. The mixture may be heated by means of a steam or water bath, but in view of the long reflux period it is better to use a hemispherical electric heating mantle controlled by a variable transformer.
6. The period of refluxing need not be continuous. A longer reflux time, up to 70 hours, does not increase the yield. The volume of the aqueous phase collected in the separating head varies from 32 to 42 ml., depending on the quality of the glycerol.

3. Discussion

Isopropylideneglycerol has been prepared from acetone and glycerol in the presence of the following acidic catalyst: hydrogen chloride,[2,3] hydrogen chloride and anhydrous sodium sulfate,[4] phosphorus pentoxide,[5] and anhydrous copper sulfate.[6] It has also been prepared from acetone and glycerol in the presence of calcium carbide and a neutral surface-active agent.[7] The two optically active isomers of isopropylideneglycerol have been prepared from 1,2,5,6-diacetone-D-mannitol and 1,2,5,6-diacetone-L-mannitol.[8] The procedure given is based on the method of Newman and Renoll.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 496

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 17, (1941).
2. Fischer, *Ber.*, **28**, 1167 (1895).
3. Irvine, Macdonald, and Soutar, *J. Chem. Soc.*, **107**, 343 (1915).
4. Fischer and Pfähler, *Ber.*, **53**, 1607 (1920).
5. Smith and Lindberg, *Ber.*, **64**, 510 (1931).
6. Hibbert and Morazain, *Can. J. Research*, **2**, 38 (1930).
7. Maglio and Burger, *J. Am. Chem. Soc.*, **68**, 529 (1946).
8. Baer and Fischer, *J. Biol. Chem.*, **128**, 468 (1939); *J. Am. Chem. Soc.*, **67**, 2035 (1945).
9. Newman and Renoll, *J. Am. Chem. Soc.*, **67**, 1621 (1945).

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

petroleum ether

calcium carbide

1,2,5,6-diacetone-D-mannitol

1,2,5,6-diacetone-L-mannitol

hydrogen chloride (7647-01-0)

sodium acetate (127-09-3)

glycerol (56-81-5)

sodium sulfate (7757-82-6)

copper sulfate (7758-98-7)

acetone (67-64-1)

isopropylideneglycerol,
dl-ISOPROPYLIDENEGLYCEROL,
Glycerol, isopropylidene-

1,3-dioxolane-4-methanol, 2,2-dimethyl- (100-79-8)

phosphorus pentoxide (1314-56-3)

p-toluenesulfonic acid monohydrate (6192-52-5)