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.

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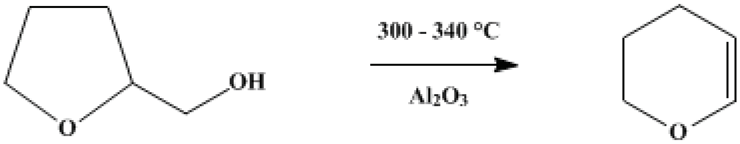
Organic Syntheses, Coll. Vol. 3, p.276 (1955); Vol. 23, p.25 (1943).

2,3-DIHYDROPYRAN

[Pyran, dihydro-]



Submitted by R. L. Sawyer and D. W. Andrus.
Checked by Nathan L. Drake and Charles M. Eaker.

1. Procedure

The reaction is carried out in a heated tube similar to that described by Herbst and Manske [*Org. Syntheses* Coll. Vol. **2**, 389 (1943)] except that the receiving chamber B (*loc. cit.*, Fig. 2) does not have a side arm, and that a 10-cm. water-cooled condenser is attached to the exit end of the tube leading directly to the receiver. The tube is packed with activated alumina (Note 1) held in place at the ends by plugs of glass wool.

The furnace is heated to 300–340° (Note 2), and 204 g. (195 ml., 2 moles) of tetrahydrofurfuryl alcohol (Note 3) is introduced from the dropping funnel at the rate of 50 ml. per hour. The product, collected in an Erlenmeyer flask which contains 30 g. of anhydrous potassium carbonate, consists of a light-brown oil and a lower aqueous layer. When the reaction tube has drained, the lower aqueous layer is separated and discarded. The upper layer is fractionated through a short column, and a fraction boiling at 70–86° is collected. This consists of a mixture of water and dihydropyran, most of which distils at 83–86°. The residue (25–35 g.) is mainly unchanged tetrahydrofurfuryl alcohol (Note 4).

The water-dihydropyran fraction separates into two layers. The lower aqueous layer is separated and discarded. The upper layer, consisting of fairly pure dihydropyran, is dried over 5–6 g. of anhydrous potassium carbonate, decanted, refluxed for 1 hour with 2–3 g. of metallic sodium, and then distilled from sodium (Note 5). The yield is 110–118 g. of dihydropyran, boiling at 84–86° (66–70%).

2. Notes

1. Several varieties of technical activated alumina were used. After three or four runs the catalyst becomes covered with a brown tar and the yield of dihydropyran decreases. The catalyst may be regenerated by igniting it at red heat until the tar is burned off. The checkers used 8–14 mesh activated alumina from the Aluminum Ore Company of America. The catalyst was reactivated at 450° by drawing a slow stream of air through it until the tar was burned off.
2. The temperature of the furnace is measured by a thermometer placed alongside the glass tube inside the furnace. The temperature should be 330–340° except in the regions about 10 cm. from each end of the furnace; here the temperatures will be 300–340°, depending on the construction of the furnace.
3. According to the submitters, Eastman's practical grade of tetrahydrofurfuryl alcohol must be purified by distillation; the fraction boiling at 79–80°/20 mm. was used. The checkers used, without purification, tetrahydrofurfuryl alcohol obtained from the Quaker Oats Company. The yields were equally good.
4. The recovered tetrahydrofurfuryl alcohol turns yellow on standing and is unsuitable for further runs. If it is used, the yield of dihydropyran drops to 36–38%, and the catalyst must be regenerated after each run.
5. Dihydropyran is very difficult to dry. Even after this treatment the product often contains traces of water.

3. Discussion

The procedure given above is essentially that of Paul.[1,2] Aluminum silicate, titanium oxide, and basic aluminum phosphate have also been used as catalysts in this rearrangement.[3] The action of sodium amide upon tetrahydrofurfuryl bromide gives chiefly 1,4-epoxy-4-pentene and a small amount of dihydropyran. 1,4-Epoxy-4-pentene undergoes rearrangement at 380° in the presence of alumina to yield dihydropyran.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 470
- Org. Syn. Coll. Vol. 3, 794
- Org. Syn. Coll. Vol. 4, 354
- Org. Syn. Coll. Vol. 4, 496

References and Notes

1. Paul, *Bull. soc. chim. France*, (4) **53**, 1489 (1933).
2. Schniepp and Geller, *J. Am. Chem. Soc.*, **68**, 1646 (1946).
3. Wilson, *J. Am. Chem. Soc.*, **69**, 3004 (1947).
4. Paul, *Bull. soc. chim. France*, (5) **2**, 745 (1935).

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

activated alumina

basic aluminum phosphate

potassium carbonate (584-08-7)

sodium (13966-32-0)

tetrahydrofurfuryl alcohol (97-99-4)

sodium amide (7782-92-5)

titanium oxide

2,3-Dihydropyran,
Pyran, dihydro-,
dihydropyran

Tetrahydrofurfuryl bromide (1192-30-9)

1,4-epoxy-4-pentene

Aluminum silicate