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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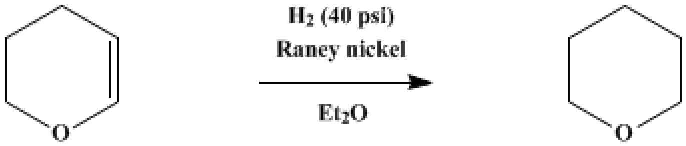
TETRAHYDROPYRAN

[Pyran, tetrahydro-]



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1. Procedure

The hydrogenation is carried out in a low-pressure catalytic hydrogenation apparatus. Raney nickel catalyst (p. 181) is washed with ether three times on a Büchner funnel, then 8 g. of it is transferred under ether to the hydrogenation bottle. The bottle is fitted with a rubber stopper bearing a small dropping funnel and a glass tube that leads to one arm of a three-way stopcock. The other arms of the stopcock are connected respectively to a water pump and a source of inert gas (Note 1) in such a way that the ether can be pumped off and the bottle can then be filled with the inert gas. When this has been done, 50.5 g. (0.6 mole) of dihydropyran (p. 276) is introduced through the dropping funnel.

The bottle is connected to the hydrogenation apparatus and alternately evacuated and filled with hydrogen twice. Hydrogen is then admitted to the system until the pressure gauge reads 40 lb. The shaker is started, and the pressure drops to the theoretical value for absorption of 0.6 mole in 15–20 minutes; beyond this point shaking causes no further absorption of hydrogen (Note 2). The bottle is removed and the nickel catalyst is allowed to settle. The tetrahydropyran is decanted, but enough is left in the bottle to cover the catalyst (Note 3). The product boils at 85–86°, but it need not be distilled for many purposes. The yield is practically quantitative.

2. Notes

1. Purified nitrogen is a convenient inert gas, but natural gas containing no oxygen, or sulfur compounds, is equally suitable; the checkers used hydrogen.
2. As the catalyst becomes older, it loses its activity somewhat and a longer time is required for the pressure to drop to the theoretical value.
3. The same catalyst may be used many times. For the next run the dihydropyran is merely poured into the bottle containing the catalyst which is wet with the product of the previous run.

3. Discussion

Tetrahydropyran has been prepared by hydrogenation of dihydropyran using a platinum black catalyst;[1] by heating pentamethylene bromide with water;[2,3] or with water and zinc oxide in a sealed tube;[4] or by heating pentamethylene glycol with 3 volumes of 60% sulfuric acid in a pressure tube,[5] or dehydration of this glycol in the vapor phase over kaolin or aluminum oxide.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 692

References and Notes

1. Paul, *Bull. soc. chim. France*, (4) **53**, 1489 (1933).

2. Hochstetter, *Monatsh.*, **23**, 1073 (1902).
3. Demjanow, *J. Russ. Phys. Chem. Soc.*, **45**, 169 (1913) [*C. A.*, **7**, 2226 (1913)].
4. Clarke, *J. Chem. Soc.*, **101**, 1802 (1912); Allen and Hibbert, *J. Am. Chem. Soc.*, **56**, 1398 (1934).
5. Demjanow, *J. Russ. Phys. Chem. Soc.*, **22**, 389 (1890) [*J. Chem. Soc.*, **62**, 1292 (1892)].
6. Beati and Mattei, *Ann. chim. appl.*, **30**, 21 (1940).

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

platinum black

kaolin

sulfuric acid (7664-93-9)

ether (60-29-7)

hydrogen (1333-74-0)

oxygen (7782-44-7)

nitrogen (7727-37-9)

sulfur (7704-34-9)

nickel,
Raney nickel (7440-02-0)

pentamethylene bromide (111-24-0)

pentamethylene glycol (111-29-5)

Tetrahydropyran,
Pyran, tetrahydro- (142-68-7)

zinc oxide

aluminum oxide (1344-28-1)

dihydropyran