



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.

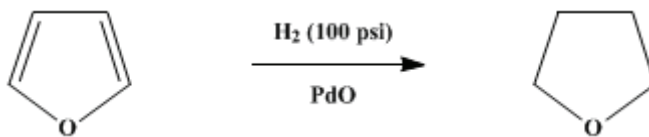
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

Organic Syntheses, Coll. Vol. 2, p.566 (1943); Vol. 16, p.77 (1936).

TETRAHYDROFURAN

[Furan, tetrahydro-]



Submitted by Donald Starr and R. M. Hixon.

Checked by John R. Johnson and H. B. Stevenson.

1. Procedure

(A) *Preparation of Palladous Oxide.*—In a 350-cc. casserole, 2.2 g. (0.02 gram atom) of palladium metal is dissolved in a small amount of aqua regia, and the solution (Note 1) is treated with 55 g. of c. p. sodium nitrate and enough distilled water to make a thick paste. The substances are thoroughly mixed and then heated gently to drive off the water. The heating is increased until the mixture melts (about 270–280°) and continued cautiously. Just above the melting point the mixture must be stirred and heated carefully as oxides of nitrogen are evolved and foaming occurs. After the evolution of gases is nearly complete (about five minutes) the full flame of a Bunsen burner is applied for about ten minutes. The entire time of heating should be about one-half hour. As the mass cools, the casserole is rotated to allow the melt to solidify on the sides of the dish. After digestion with about 200 cc. of distilled water until the sodium salts are completely dissolved, the dark brown precipitate of palladous oxide is filtered and washed thoroughly with 1 per cent sodium nitrate solution (Note 2). The oxide must not be washed with pure water since it shows a marked tendency to become colloidal. After drying in a vacuum desiccator the palladous oxide weighs 2.3–2.4 g. (91–95 per cent of the theoretical amount) (Note 3).

(B) *Tetrahydrofuran.*—In the pressure bottle of an apparatus for catalytic reduction (Note 4) are placed 10 g. of pure furan (Note 5) and 0.2 g. of palladous oxide. The bottle is swept out with hydrogen (Note 6), and an initial hydrogen pressure of about 7 atm. (100 lb.) is applied (Note 7). After a lag of about ten minutes the reduction proceeds smoothly, and in an hour the theoretical amount of hydrogen is absorbed; the reaction is noticeably exothermic. After the reaction has ceased 20 g. of furan and 0.2 g. of palladous oxide are added (Note 6), the bottle swept out with hydrogen, and the hydrogen pressure raised to 7 atm. After this addition the lag is short and the reaction proceeds somewhat more rapidly than before; the temperature rises to 40–50°. When the reaction nears completion, 30 g. of furan and 0.2 g. of palladous oxide are added, and the reduction is continued. Successive portions of 30 g. of furan and 0.2 g. of palladous oxide are added in the same manner, until the bottle is about two-thirds filled. To ensure complete reduction, another portion of palladous oxide is added and the mixture shaken until no more hydrogen is taken up. The catalyst is allowed to settle (Note 8), and the tetrahydrofuran is decanted through a filter into a flask for distillation. The reduction product distills completely at 64–66°.

The reduction of 120 g. (128 cc., 1.76 moles) of furan requires about fifteen to twenty hours, depending upon the purity of the furan and the activity of the catalyst (Note 9). The yield of redistilled tetrahydrofuran is 114–118 g. (90–93 per cent of the theoretical amount). Since reduction is practically quantitative, the yield is determined largely by the care exercised in handling the volatile furan and tetrahydrofuran.

2. Notes

1. An aqueous solution of the equivalent quantity of Eimer and Amend's c.p. or Merck's reagent palladium chloride may be used.
2. The filtrates should be clear and colorless; if they show a yellow-orange opalescence, some of the oxide has become colloidal. The palladium may be recovered¹ as the oxide by evaporating the filtrates to dryness and re-fusing, or as palladium black by rendering the filtrates slightly alkaline with sodium

carbonate and heating with formaldehyde.

3. A small amount of palladous oxide adheres to the casserole and cannot be removed by the ordinary means. The oxide is not dissolved readily by aqua regia but is easily removed by boiling with 48 per cent hydrobromic acid.

4. If initial pressures of 6–7 atm. are to be applied, the ordinary apparatus for catalytic reduction (*Org. Syn. Coll. Vol. I, 1941, 61*) must be modified by using a flexible coil of copper tubing instead of rubber tubing for the connection between the hydrogen tank and the reduction bottle. To avoid dangerous accidents and loss of materials, it is advisable to cover the reduction bottle at all times with a screen of wire mesh and to test the bottle at the higher pressures before use. Brass fittings are used to hold the mouth of the bottle against a rubber gasket; before use the gasket is treated with alkali, washed thoroughly, and dried.

5. As in all catalytic reductions, the purity of the starting material is of great importance. Redistilled furan, b.p. 31–32°, prepared by the method of Wilson (*Org. Syn. Coll. Vol. I, 1941, 274*) is quite satisfactory. It has been reported that furan prepared by the method of Gilman and Louisinian² should be dried over calcium chloride and fractionated carefully.³ It is advisable to redistil the furan shortly before use and to avoid contact with rubber stoppers.

6. Owing to the high volatility of furan and tetrahydrofuran the bottle is not evacuated, as is customary, before the hydrogen pressure is applied; instead, the air is displaced by hydrogen. For the same reason, appreciable losses will occur if the reduction bottle is not cooled before the hydrogen pressure is released for the introduction of fresh portions of furan and catalyst. Effective and rapid cooling may be obtained by directing a jet of ether, from a wash bottle, over the surface of the reduction bottle while the shaking motor is in operation.

7. The hydrogenation of furan may be carried out with initial pressures of only 3 atm. (45 lb.), but the reduction is slower.

8. The catalyst may be removed, dried in a vacuum desiccator over sulfuric acid, and used again. The second reduction usually proceeds much more slowly, and it is advantageous to use one or two portions of fresh oxide along with the recovered material. Spent catalyst may be regenerated by conversion to the oxide as described in Part (A).

9. In the high-pressure apparatus of Adkins, 120 g. of furan can be hydrogenated with 10 g. of Raney nickel catalyst⁴ in a single run. Using pressures of 100–150 atm. and a temperature range of 100–150° the reduction is extremely rapid and is strongly exothermic. Platinum oxide-platinum black is not a satisfactory catalyst for the reduction of furan.³

3. Discussion

The preparation of palladous oxide-palladium black and its use as a catalyst in the reduction of organic compounds have been studied by Shriner and Adams.¹ Palladium black and colloidal palladium have been widely used as hydrogenation catalysts.⁵

Tetrahydrofuran has been prepared by the reduction of furan in the vapor phase with a nickel catalyst at 170°,⁶ in butyl alcohol at 50° with Raney nickel catalyst,⁷ with palladous oxide-palladium black in the absence of a solvent,³ and with an osmium-asbestos catalyst;⁸ by the reduction of an alkyl succinate over a copper chromite catalyst;⁹ and by the dehydration of 1,4-butylene glycol.¹⁰

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2, 571*
- *Org. Syn. Coll. Vol. 5, 60*

References and Notes

1. Shriner and Adams, *J. Am. Chem. Soc.* **46**, 1684 (1924); Kern, Shriner, and Adams, *ibid.* **47**, 1147 (1925).
2. Gilman and Louisinian, *Rec. trav. chim.* **52**, 156 (1933).
3. Starr and Hixon, *J. Am. Chem. Soc.* **56**, 1595 (1934).

4. Covert and Adkins, *ibid.* **54**, 4116 (1932).
 5. Sabatier, "Catalysis in Organic Chemistry," transl. by E. Emmet Reid. New York, D. Van Nostrand Company, 1922.
 6. Bourguignon, *Bull. soc. chim. Belg.* **22**, 88 (1908); Shuikin and Bunina, *J. Gen. Chem. (U.S.S.R.)* **8**, 669 (1938) [*C. A.* **33**, 1316 (1939)].
 7. Cloke and Ayers, *J. Am. Chem. Soc.* **56**, 2144 (1934).
 8. Shuikin and Chilikina, *J. Gen. Chem. (U.S.S.R.)* **6**, 279 (1936) [*C. A.* **30**, 4855 (1936)].
 9. E. I. du Pont de Nemours and Company, U.S. pat. 2,130,501 [*C. A.* **32**, 9101 (1938)].
 10. Strukov, *Khim. Farm. Prom.* **1935**, No. 1, 35 [*C. A.* **30**, 1769 (1936)]; General Aniline and Film Corporation, U. S. pat. 2,251,292 [*C. A.* **35**, 6982 (1941)]; I. G. Farbenind. A.-G., Ger. pat. 700,036 [*C. A.* **35**, 6982 (1941)].
-

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

oxides of nitrogen

palladium black

platinum oxide-platinum black

Palladous oxide-palladium black

aqua regia

Eimer and Amend's c.p. or Merck's reagent palladium chloride

colloidal palladium

osmium-asbestos

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ether (60-29-7)

hydrogen (1333-74-0)

formaldehyde (50-00-0)

HYDROBROMIC ACID (10035-10-6)

sodium carbonate (497-19-8)

butyl alcohol (71-36-3)

nickel,
Raney nickel (7440-02-0)

palladium (7440-05-3)

Furan (110-00-9)

sodium nitrate

Palladous oxide

COPPER CHROMITE

Tetrahydrofuran,
Furan, tetrahydro- (109-99-9)

1,4-butyleneglycol