



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.

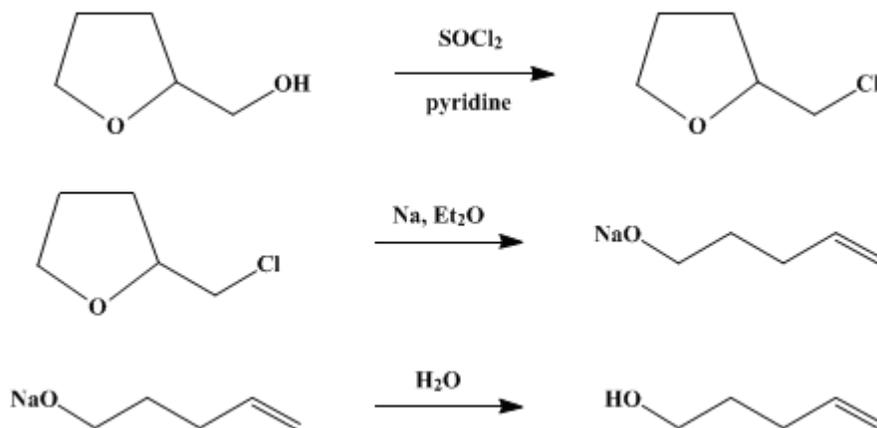
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures 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. 3, p.698 (1955); Vol. 25, p.84 (1945).

4-PENTEN-1-OL



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1. Procedure

A. *Tetrahydrofurfuryl chloride*. In a 2-l. three-necked flask, fitted with a mechanical stirrer, a dropping funnel, and a thermometer, are placed 408 g. (4 moles) of freshly distilled [tetrahydrofurfuryl alcohol](#) (Note 1) and 348 g. (4.4 moles) of [pyridine](#). To the rapidly stirred mixture, which is cooled in an ice bath, 500 g. (4.2 moles) of freshly distilled [thionyl chloride](#) (Note 1) is added from the dropping funnel at the rate of 3–5 drops per second. When one-third to one-half of the [thionyl chloride](#) has been added, a pasty crystalline mass begins to separate and the temperature begins to rise rapidly. The temperature should not be allowed to go above 60°. As more [thionyl chloride](#) is added the mass redissolves and a dark brown liquid forms. When the addition is complete, the bath is removed and the mixture is stirred for 3–4 hours. The liquid (or the slurry, if some crystallization has occurred) is poured into a beaker (Note 2) and extracted seven times with 500-ml. portions of [ether](#) (Note 3); the [ether](#) extracts are decanted and combined. The [ether](#) is removed by distillation, and the residue is washed three times with 100-ml. portions of water, dried over anhydrous [magnesium sulfate](#), and distilled under reduced pressure. The yield of [tetrahydrofurfuryl chloride](#) boiling at 41–42° /11 mm. (47–48° /15 mm.) is 354–360 g. (73–75%).

B. *4-Penten-1-ol*. A 2-l. three-necked flask containing 112 g. (4.87 moles) of powdered [sodium](#) (Note 4) under 700 ml. of anhydrous [ether](#) is fitted with a mechanical stirrer, a separatory funnel, and a reflux condenser with a drying tube. A few milliliters (2–3) of a mixture of 300 g. (2.5 moles) of [tetrahydrofurfuryl chloride](#) and 300 ml. of anhydrous [ether](#) is added to the rapidly stirred suspension. A vigorous reaction occurs, and the solution turns blue. The remainder of the solution of the chloride is then added dropwise over a period of 5 hours, during which time the flask is cooled in an ice bath (Note 5). When the addition is complete, stirring is continued for 2 hours. The suspension is decanted from any [sodium](#) that remains (Note 6) into a dry beaker and decomposed with sufficient ice water to give two liquid layers. The [ether](#) layer is separated and dried over [magnesium sulfate](#). After the removal of the ether by distillation on a steam cone, the residue is distilled. The yield of [4-penten-1-ol](#) boiling at 134–137° is 161–178 g. (76–83%).

2. Notes

- Undistilled commercial [thionyl chloride](#) and Eastman practical [tetrahydrofurfuryl alcohol](#) may be used, but the yields are slightly lower (65–70%).
- The checkers found it easier to separate the ethereal extract from the residue when the mixture was in a large separatory funnel.

3. The yield will be low if extraction is incomplete. It is advisable to stir with a heavy glass rod and break up any lumps that have formed.
4. The powdered [sodium](#) is prepared under hot [xylene](#) with the aid of a Hershberg stirrer; the [xylene](#) is decanted and replaced with [ether](#).
5. The ice bath is not used until the reaction has definitely started.
6. Occasionally a little [sodium](#) is left on the bottom of the flask. This is destroyed with [ethanol](#) and the flask is washed with ice water.

3. Discussion

[Tetrahydrofurfuryl chloride](#) has been prepared from the alcohol and [thionyl chloride](#)¹ or [phosphorus trichloride](#). [4-Penten-1-ol](#) has been prepared from tetrahydrofurfuryl bromide or chloride and [magnesium](#),^{2,3} [sodium](#),^{4,5,6} [sodium-potassium](#),⁶ or [lithium](#);⁶ and by the reaction of [allylmagnesium chloride](#) with [ethylene oxide](#), followed by hydrolysis.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 755](#)
- [Org. Syn. Coll. Vol. 6, 675](#)

References and Notes

1. Kirner, *J. Am. Chem. Soc.*, **52**, 3251 (1930).
 2. Paul, *Bull. soc. chim. France*, (4) **53**, 424 (1933).
 3. Robinson and Smith, *J. Chem. Soc.*, **1936**, 195.
 4. Paul, *Bull. soc. chim. France*, (5) **2**, 745 (1935).
 5. Gaubert, Linstead, and Rydon, *J. Chem. Soc.*, **1937**, 1971.
 6. Paul and Normant, *Bull. soc. chim. France*, (5) **10**, 484 (1943).
 7. Kharasch and Fuchs, *J. Org. Chem.*, **9**, 359 (1944).
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Appendix

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

tetrahydrofurfuryl bromide or chloride

[ethanol](#) (64-17-5)

[ether](#) (60-29-7)

[thionyl chloride](#) (7719-09-7)

[magnesium](#) (7439-95-4)

[pyridine](#) (110-86-1)

[sodium](#) (13966-32-0)

[phosphorus trichloride](#) (7719-12-2)

Ethylene oxide (75-21-8)

xylene (106-42-3)

tetrahydrofurfuryl alcohol (97-99-4)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

4-Penten-1-ol (821-09-0)

Tetrahydrofurfuryl chloride (3003-84-7)

sodium-potassium

Allylmagnesium chloride (2622-05-1)