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.

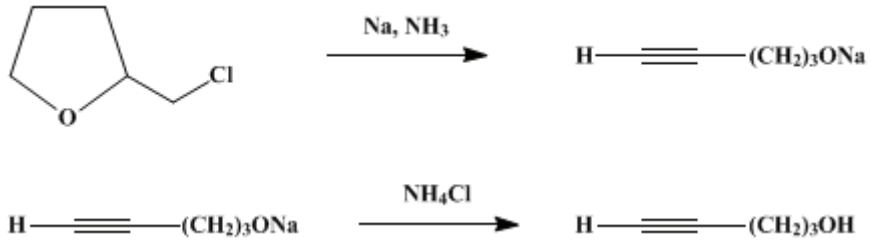
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.033.0068

Organic Syntheses, Coll. Vol. 4, p.755 (1963); Vol. 33, p.68 (1953).

4-PENTYN-1-OL



Submitted by E. R. H. Jones, Geoffrey Eglinton, and M. C. Whiting[1].
Checked by Arthur C. Cope and Ronald M. Pike.

1. Procedure

Caution! This preparation should be conducted in a hood to avoid exposure to ammonia.

A solution of sodium amide in liquid ammonia is prepared according to a procedure previously described (Note 1) in a 3-l. three-necked round-bottomed flask equipped with a cold-finger condenser (cooled with Dry Ice) attached through a soda-lime tower to a gas-absorption trap,[2] a mercury-sealed stirrer, and an inlet tube. Anhydrous liquid ammonia (1 l.) is introduced from a commercial cylinder through the inlet tube, and 1 g. of hydrated ferric nitrate is added, followed by 80.5 g. (3.5 g. atoms) of clean, freshly cut sodium (Note 1) and (Note 2). The inlet tube is replaced with a 250-ml. dropping funnel, and the mixture is stirred until all the sodium is converted into sodium amide, after which 120.5 g. (1 mole) of tetrahydrofurfuryl chloride[3] (Note 3) is added over a period of 25 to 30 minutes. The mixture is stirred for an additional period of 1 hour, after which 177 g. (3.3 moles) of solid ammonium chloride is added in portions at a rate that permits control of the exothermic reaction. The flask is allowed to stand overnight in the hood while the ammonia evaporates. The residue is extracted thoroughly with ten 250-ml. portions of ether, which are decanted through a Büchner funnel (Note 4). The ether is distilled, and the residue is fractionated at a reflux ratio of about 5 to 1, through a column containing a 20-cm. section packed with glass helices yielding 63–71 g. (75–85%) of 4-pentyn-1-ol, b.p. 70–71° /29 mm., n_D^{25} 1.4443 (Note 5).

2. Notes

1. Procedures for converting sodium to sodium amide are given on p. 763 and in a previous volume.[4]
2. More liquid ammonia should be added through the inlet tube if vaporization reduces the liquid volume to less than 750 ml.
3. Freshly distilled tetrahydrofurfuryl alcohol should be used in the preparation of tetrahydrofurfuryl chloride according to the procedure of *Organic Syntheses*.[3]
4. Ether extraction of the solid must be thorough or the yield will be reduced. A large Soxhlet extractor may be used if desired.
5. Others have reported b.p. 154–155°, n_D^{19} 1.4432;[5] b.p. 154–155°, $n_D^{22.5}$ 1.4450.[6] A sample purified through the silver derivative had b.p. 77° /37 mm., n_D^{15} 1.4464. The α-naphthylurethan of 4-pentyn-1-ol crystallized as needles from 60–80° petroleum ether; m.p. 79–80°.

3. Discussion

4-Pentyn-1-ol has been prepared from 4-penten-1-ol[3] by bromination followed by dehydrobromination with alkali;[6] by the reaction of 3-bromodihydropyran or 3,4-dihydro-2H-pyran with *n*-butylsodium, *n*-butyllithium, or *n*-butylpotassium;[5,7] by the reaction of dihydropyran or 2-methylenetetrahydrofuran with *n*-amylsodium or *n*-butyllithium;[7] by the reduction of ethyl 4-pentynoate with lithium aluminum hydride;[8] and by the method used in this preparation.[9]

References and Notes

1. Victoria University of Manchester, Manchester, England.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. *Org. Syntheses Coll. Vol.* **3**, 698 (1955).
4. *Org. Syntheses Coll. Vol.* **3**, 219 (1955).
5. Paul and Tchelitcheff, *Compt. rend.*, **230**, 1473 (1950); Paul, *Angew. Chem.*, **63**, 304 (1951); Paul, *Bull. soc. chim. France*, **18**, 109 (1951).
6. Lespieau, *Compt. rend.*, **194**, 287 (1932).
7. Paul and Tchelitcheff, *Bull. soc. chim. France*, **19**, 808 (1952).
8. Colonge and Gelin, *Bull. soc. chim. France*, **1954**, 799.
9. Eglinton, Jones, and Whiting, *J. Chem. Soc.*, **1952**, 2873.

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

petroleum ether

α-naphthylurethan of 4-pentyn-1-ol

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium (13966-32-0)

tetrahydrofurfuryl alcohol (97-99-4)

sodium amide (7782-92-5)

n-butyllithium (109-72-8)

ferric nitrate

lithium aluminum hydride (16853-85-3)

dihydropyran

2-methylenetetrahydrofuran

n-amylsodium

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

Tetrahydrofurfuryl chloride (3003-84-7)

4-Pentyn-1-ol (5390-04-5)

3-bromodihydropyran

3,4-dihydro-2H-pyran (110-87-2)

ethyl 4-pentynoate (63093-41-4)

n-butylsodium

n-butylpotassium