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.

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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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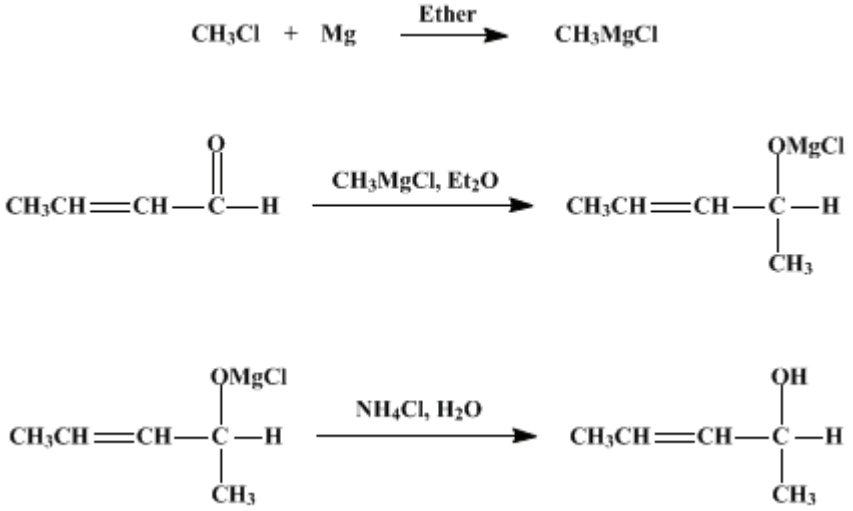
3-PENTEN-2-OL



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1. Procedure

A 5-l. round-bottomed three-necked flask is equipped with a mechanical stirrer in a suitable seal (Note 1), a reflux condenser of the cold-finger type (Note 2) protected from moisture in the air by a drying tube, and a gas delivery tube extending nearly to the bottom of the flask. The flask is surrounded by an ice bath, and the cold finger is filled with solid carbon dioxide in acetone. Approximately 1.7 l. of dry ether and 61 g. (2.5 gram atoms) of magnesium are placed in the flask and cooled to about 0°. Methyl chloride (130 ml., 130 g., 2.6 moles) is condensed (Note 3) in a 250- to 300-ml. test tube held in a bath of solid carbon dioxide in acetone (Note 4). About 50 ml. of methyl chloride is allowed to distil from the test tube containing the methyl chloride through the gas delivery tube into the rapidly stirred mixture of ether and magnesium. The reaction mixture is then warmed until the reaction of methyl chloride and magnesium is under way. A crystal of iodine may be added if the reaction does not start readily. The methyl chloride is then allowed to distil into the reaction mixture during a period of about 3 hours. The reaction mixture and the tube containing the methyl chloride are cooled if the refluxing of the reaction mixture becomes so vigorous that the reflux condenser does not condense the methyl chloride. After all the methyl chloride has been added, the reaction mixture is warmed for 1 hour so that there is a gentle reflux.

At the end of this time, when almost all the magnesium has reacted, the Dry Ice cold finger is replaced with a water condenser and the gas delivery tube with a dropping funnel. A solution of 142 g. (2.02 moles) of freshly distilled crotonaldehyde in 300 ml. of dry ether is added dropwise while the reaction mixture is stirred vigorously and cooled. The reaction mixture is allowed to stand at room temperature for 1 hour.

The Grignard addition compound is decomposed by adding 435 ml. of a saturated ammonium chloride solution (Note 5) dropwise, with vigorous stirring, to the thoroughly cooled reaction mixture. A dense white precipitate, too heavy to be stirred mechanically, forms and settles to the bottom of the flask. After the reaction mixture has been allowed to stand for 1 hour, the ether solution is poured off and the precipitate washed by decantation with two 300-ml. portions of ether.

The ether is removed by distillation, and the residual 3-penten-2-ol is distilled through a short column (Note 6) at atmospheric pressure. The yield of material boiling at 119–121° is 140–150 g. (81–86%). Pure 3-penten-2-ol boils at approximately 120°/740 mm.

2. Notes

1. A Hershberg type of stirrer is preferred. The submitter used a stirrer of tantalum with a mercury seal; the checkers used a Nichrome stirrer in a simple rubber seal.
2. The reflux condenser must be of very high capacity, as otherwise methyl chloride may be lost. The checkers used a cold-finger type of condenser in which the dimensions of the finger or container for the refrigerant were 30 cm. in length and 3 cm. in outside diameter. The glass jacket surrounding the finger was 4.5 cm. in outside diameter, but was drawn down to 1.3 cm. below the finger for convenience of insertion into one of the necks of the reaction flask.
3. Methyl chloride is led from a commercial cylinder to the bottom of the test tube used for measuring and storing the reagent. The tube is previously marked so that the desired volume (130 ml.) of methyl chloride may be readily measured.
4. The checkers also obtained equally good results with less effort by allowing a slow stream of dry methyl chloride to pass directly from the commercial cylinder into the reaction mixture until practically all the magnesium had reacted.
5. Hydrolysis of the Grignard complex with saturated ammonium chloride solution possesses the advantage that the resulting ethereal solution of the alcohol is neutral and sufficiently dry so that it need not be dried before distillation. The alcohol is dehydrated if it is distilled from a mixture containing even a trace of a mineral acid. Approximately 125 g. of ammonium chloride and 345 ml. of water are required for the saturated solution referred to above.
6. The submitter used a Hempel column. The checkers used a modified Widmer or Vigreux column, 1.3 cm. in diameter and 15 cm. in length.

3. Discussion

3-Penten-2-ol has been prepared by the addition of methylmagnesium iodide[1,2] or bromide[3,4,5,6] to crotonaldehyde and by the partial dehydration of pentanediol,[7] and by the hydrolysis of 2-chloropentene-3.[8]

References and Notes

1. Courtot, *Bull. soc. chim. France*, (3) **35**, 983 (1906).
2. Kyriakides, *J. Am. Chem. Soc.*, **36**, 663 (1914).
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5. Auwers and Westermann, *Ber.*, **54**, 2996 (1921).
6. Hurd and Cohen, *J. Am. Chem. Soc.*, **53**, 1917 (1931).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium (7439-95-4)

carbon dioxide (124-38-9)

methyl chloride (74-87-3)

iodine (7553-56-2)

acetone (67-64-1)

methylmagnesium iodide (917-64-6)

crotonaldehyde (123-73-9)

3-Penten-2-ol (1569-50-2)

pentanediol

2-chloropentene-3