



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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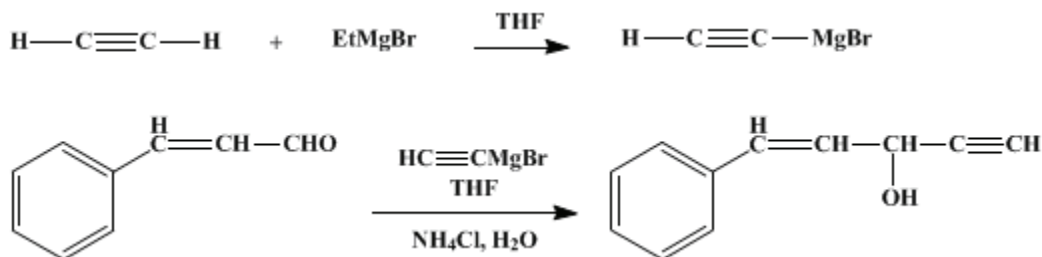
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.792 (1963); Vol. 39, p.56 (1959).

1-PHENYL-1-PENTEN-4-YN-3-OL

[1-Penten-4-yn-3-ol, 1-phenyl-]



Submitted by Lars Skattebøl, E. R. H. Jones, and Mark C. Whiting¹.

Checked by Melvin S. Newman and Raymond E. Dessy.

1. Procedure

A. *Ethynylmagnesium bromide*. A 500-ml. three-necked flask, equipped with a sealed mechanical stirrer, a reflux condenser, and a pressure-equalized dropping funnel, is arranged for carrying out a reaction in an atmosphere of **nitrogen** by fitting into the top of the condenser a T-tube attached to a low-pressure supply of **nitrogen** and to a mercury bubbler. For later use there is also prepared a dry 1-l. three-necked flask equipped with a sealed mechanical stirrer, a gas inlet tube which will dip below the surface of 200 ml. of liquid in the flask, a 500-ml. dropping funnel, and a gas outlet protected by a calcium chloride drying tube.

The 500-ml. flask is dried by warming with a soft flame as a slow stream of **nitrogen** is passed through the system. A solution of *ethylmagnesium bromide* is prepared in this flask from 12 g. (0.5 g. atom) of **magnesium turnings**, 60 g. (0.55 mole) of *ethyl bromide* (dried over **calcium chloride**), and 300 ml. of **tetrahydrofuran** (Note 1) and (Note 2).

After the preparation of *ethylmagnesium bromide* is completed, the separatory funnel is replaced by a bent tube which reaches the bottom of the flask and is bent at the outer end for downward delivery (Note 3). The warm (40–50°) solution is forced under **nitrogen** pressure (by carefully pinching off the tube to the mercury bubbler) into the 500-ml. separatory funnel which has been prepared for attachment to the 1-l. flask. After all the solution has passed into the separatory funnel, **nitrogen** flow is allowed to continue briefly in order to displace the air above the solution, then the funnel is stoppered loosely and attached to the 1-l. flask. Two hundred milliliters of purified **tetrahydrofuran** is now placed in the flask, **acetylene** (Note 4) is introduced through the gas-inlet tube at the rate of 15–20 l. per hour, and the stirrer is started. After 5 minutes, about 5 ml. of the solution of *ethylmagnesium bromide* is added in 1 portion. Almost at once, there appears a froth of **ethane** which is easily distinguishable from the larger bubbles of **acetylene**. When the frothing subsides, portionwise addition of the *ethylmagnesium bromide* solution is continued until the total solution has been added. This requires about 3 hours, and the temperature of the reaction rises 5–10° above room temperature. The solution of *ethynylmagnesium bromide* is homogeneous at 30° (Note 5).

B. *1-Phenyl-1-penten-4-yn-3-ol*. The stirred solution of *ethynylmagnesium bromide* is cooled in ice water as there is added dropwise during about 45 minutes a solution of 47.5 g. (0.36 mole) of freshly distilled **cinnamaldehyde** (Note 6) in 50 ml. of purified **tetrahydrofuran**. After addition is complete, stirring is continued overnight as the solution is allowed to warm to room temperature. The brown homogeneous reaction mixture is added carefully to 1.5 l. of cooled saturated **ammonium chloride** solution, then the aqueous phase is extracted with three 250-ml. portions of **ether**. The **ether** extracts are combined with the **tetrahydrofuran** solution and dried over anhydrous **magnesium sulfate**. After evaporation of the solvent, the product is distilled (Note 7) at a pressure of about 0.1 mm., with the heating bath at about 90°. The distillate, which solidifies on cooling, is crystallized from petroleum

ether (b.p. 40–60°) to yield 33–39 g. (58–69%) of the unsaturated alcohol of m.p. 67–68° (Note 8).

2. Notes

1. If less solvent is used, the ethylmagnesium bromide may crystallize on cooling.
2. If ether is substituted for tetrahydrofuran in this preparation, the acetylenic glycol is the sole product. The submitters purified the tetrahydrofuran by shaking with potassium hydroxide pellets, heating under reflux with sodium metal, and finally distilling. They report that heating under reflux with sodium diphenylketyl gives a better sample of tetrahydrofuran, but that this does not improve the yield. The checkers purified the solvent by shaking with potassium hydroxide, distilling from lithium aluminum hydride, then storing over sodium wire.
3. It is advisable to prepare the delivery tube prior to its need.
4. The submitters purified the acetylene by passing it through a trap cooled to –80°, then through concentrated sulfuric acid, and finally through soda-lime. The checkers purified the acetylene by passing it first through a tower of 10-mesh alumina, then through concentrated sulfuric acid.
5. No outside cooling is employed during the preparation of ethynylmagnesium bromide. If this solution of ethynylmagnesium bromide is cooled to 0°, a crystalline complex separates. If part of the solvent is evaporated, even at 40° under reduced pressure, there occurs disproportionation to acetylene and the bisbromomagnesium derivative.
6. Methyl ethyl ketone, crotonaldehyde, and acrolein react similarly with ethynylmagnesium bromide. The respective yields of acetylenic alcohols are 69%, 84%, and 40%.
7. The submitters used a still of the evaporative type, such as a Hickman still. The checkers used a similar still modified to include a magnetic stirring bar. This modification greatly decreases the time required for removal of the last traces of solvent, minimizes the danger of bumping just before evaporative distillation occurs, and increases the rate of distillation of the product.
8. The checkers report yields as high as 84% and believe that the use of magnetic stirring in the Hickman still is responsible for the higher yield.

3. Discussion

The preparation of ethynylmagnesium bromide in ether has been described;^{2,3} however, the subsequent history of the compound has been controversial. The submitters have been unable to prepare ethynylcarbinols by the earlier procedures.

1-Phenyl-1-penten-4-yn-3-ol has been prepared in liquid ammonia from cinnamaldehyde and sodium acetylides in 2% yield,⁴ and from the sodium bisulfite compound of cinnamaldehyde and sodium acetylides in 13.5% yield.⁵ The present procedure has been published.⁶

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 258
- Org. Syn. Coll. Vol. 8, 606
- Org. Syn. Coll. Vol. 5, 976

References and Notes

1. The Dyson Perrins Laboratory, Oxford, England.
 2. Salkind and Rosenfeld, *Ber.*, **57**, 1690 (1924).
 3. Grignard, Lapayre, and Tcheou, *Compt. rend.*, **187**, 517 (1928).
 4. Jones and McCombie, *J. Chem. Soc.*, **1942**, 733.
 5. Cymerman and Wilks, *J. Chem. Soc.*, **1950**, 1208.
 6. Jones, Skattebøl, and Whiting, *J. Chem. Soc.*, **1956**, 4765.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

petroleum ether

soda-lime

sodium diphenylketyl

sodium bisulfite compound of cinnamaldehyde

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

acetylene (74-86-2)

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

Acrolein (107-02-8)

magnesium turnings (7439-95-4)

Ethyl bromide (74-96-4)

nitrogen (7727-37-9)

potassium hydroxide (1310-58-3)

sodium,
sodium wire (13966-32-0)

cinnamaldehyde

ethylmagnesium bromide (925-90-6)

magnesium sulfate (7487-88-9)

ethane (74-84-0)

methyl ethyl ketone (78-93-3)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

sodium acetylide

crotonaldehyde (123-73-9)

ethynylmagnesium bromide

1-Phenyl-1-penten-4-yn-3-ol,
1-Penten-4-yn-3-ol, 1-phenyl- (14604-31-0)