Addition of Allyl Magnesium Chloride to Propynal; 5-Hexen-1-yn-3-ol

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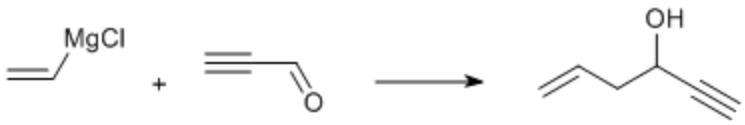

Chemicals Used

Magnesium, chip, 99.98%, Sigma Aldrich
Allyl Chloride, freshly distilled, 99%, Sigma Aldrich
Diethyl Ether, 99.9%, Sigma Aldrich
Propynal, Prepared by the Organic Synthesis Procedure, see other reference below,
Ammonium Chloride, 99.5%, Sigma Aldrich
Tetrahydrofuran, 99.5%, Sigma Aldrich

Procedure

In a 1 liter three neck flask, equipped with mechanical stirrer, Y tube, dropping funnel, nitrogen inlet, and Friedrich water condenser, were placed 300 ml of dry ether and 34 g (1.4 mole) of magnesium turnings while maintaining the system under dry nitrogen. A crystal of iodine was added to initiate Grignard activation, followed by a solution of 54 g (0.7 mole) of redistilled allyl chloride in 100 ml ether, which was added dropwise, with stirring, over a period of two hours. During the course of the addition a thick white Grignard complex precipitated which was redissolved by addition of 1 ml dry tetrahydrofuran. After the addition was complete, the flask was immersed in a dry ice/ acetone bath at -25° to -30°. Then 11 g (0.2 mole) of freshly prepared proynal in 100 ml ether was added, dropwise, over a period of one hour, while the bath temperature was maintained as above. After the addition the mixture was allowed to warm to room temperature and was decomposed by pouring over a slurry of 500g ammonium chloride and 500 g ice in a two liter beaker. The ether and aqueous layer were separated and the aqueous layer was extracted twice with 50 ml ether portions. The combined ether extracts were shaken with 20 ml of water and then were dried over 25 g anhydrous magnesium sulfate for one hour. The ether solution was decanted off into a one liter beaker. Removal of the ether on a steam bath yielded a light yellow oil. The oil was distilled, under aspirator pressure, in an oil bath, 35 mm pressure, bath temperature ~100 °and the fraction boiling at 67-69° , (35 mm) was collected and appeared to be homogeneous by gas chromatography, 5-ft-SE-30 column, 100 °.column temperature.The yield of 5-hexen-1-yn-3-ol was 11 g (57% based upon the amount of propynal used). Other runs gave yields typically in the 50-60% range.

Author's Comments

Propynal and allyl chloride are potent lachrimators! They, together with propargyl alcohol, are also toxic. Always work with them in an efficient fume hood with gloves and safety glasses. Propynal is also unstable, and should be used immediately after synthesis if possible. It may be stored at 0° in an ice chest if necessary, for several days with no apparent significant decomposition..

Data

n_D^{21} 1.4580, d_4^{25} 0.8953.

Analysis: Calculated for C_6H_8O: C,74.97; H, 8.39. Found: C,74.93; H, 8.42.

IR (neat) 3400(s, broad, OH stretch), 3300(s, sharp, terminal alkyne stretch overlaps OH stretch), 3080(m), 2900(m), 2130(w), 1650(m), 1435(m), 1300(m), 1260(w), 1220(w), 1120(m), 1030(s), 990(s), 955(m), 920(s), 880(w), 865(w), 800(w), and 640(s) cm^{-1}.

1H NMR (CDCl3.) 60 Mhz, δ 2.5 (4H, m, allylic, acetylenic and hydroxylic), which collapsed to a simpler multiplet , (3H, allylic and acetylenic),on D_2O exchange, 4.43 (1H,m, methine), 5.2 (2H, m, terminal vinyl) and 5.9 (1H, m, internal vinyl).

Lead Reference

A. Viola and J. H. MacMillan, "The Vapor Phase Acetylenic oxy-Cope Reaction of 5-Hexen-1-yn-3-ol, The Chemistry of an Allenol Intermediate", J. Am. Chem. Soc., 92, 2404 (1970).
DOI: 10.1021/ja00711a034

Other References

Propynal Synthesis, see J.C. Sauer, Organic Syntheses, Coll. Vol. 4, p.813 (1963); Vol. 36, p.66 (1956).

Get structure file (.cdx, .sk2, .mol)

Keywords: addition, **alcohols**, **aldehydes**, **alkynes**, **nucleophilic**, **organometallics**