Reduced pressure oxidation of propargyl alcohol to aldehyde; Propynal

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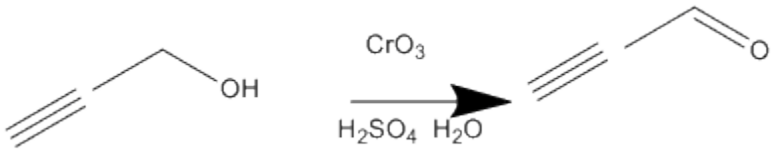

Chemicals Used

Propargyl alcohol, 99%, Aldrich, P5,080-3, redistilled
Chromium (VI) oxide, 99+%, Aldrich, 20,782-9
Sodium Chloride, 99%*%, A.C.S. reagent, Aldrich, 22,351-4
Sulfuric acid, 95-98%, A.C.S. Reagent, Aldrich, 25.810-5

Procedure

This material was prepared by a modification of the Organic Synthesis procedure. See lead reference.

To a 2 liter three neck flask, equipped with a mechanical stirrer, and ice/salt bath was charged 120 g ((2.14 mole) redistilled propargyl alcohol and 240 ml of water. To this mixture was then added a cooled solution of 135 ml concentrated sulfuric acid in 150 ml of water. A "Y" tube was inserted in one neck of the flask and a pressure equalized dropping funnel was placed in one neck of the "Y" tube. The other neck of the "Y" tube lead to two traps, in series, which in turn were connected to a McLeod pressure gage and vacuum pump. The third neck of the flask was connected to a fine capillary which served as a nitrogen inlet. A cooled solution of 210 g chromium trioxide, 200 ml of water and 100 ml concentrated sulfuric acid was then added to the dropping funnel. One trap was cooled to ~ - 10° with an ice/salt mixture and the second trap was cooled with a dry ice/acetone bath to ~ -78°C. The exterior of the 2 liter flask was cooled to ~ -10°C with ice/salt. Nitrogen was introduced through the capillary and the pressure of the system was reduced to 15 mm. The chromium trioxide-acid solution was added, with stirring, over a three hour period, while the temperatures in the baths were maintained as mentioned. After the addition was complete, the pressure of the system was reduced to 5 mm for fifteen minutes. Vacuum was released and the material in the traps allowed to reach room temperature. The liquids in the traps were combined and the material saturated with sodium chloride. At this point an upper organic layer separated from the solution. The upper organic layer was separated via a small separatory funnel, dried over 5g magnesium sulfate for one hour, decanted, then carefully fractionated at atmospheric pressure with a short path (16 inch) column. The material boiling between 54-58° C(760mm) was collected and shown to be homogeneous by g.c. (5 ft SE-30 column).

Yields varied from 20 g to 35 g (17 to 30%) depending upon the efficiency of the vacuum system. This synthesis is suitable for oxidizing lower boiling unsaturated alcohols to aldehydes without further oxidation to carboxylic acid or cleavage of the unsaturated bonds.

Author's Comments

Caution, run this reaction in an efficient fume hood. Both propynal and propargyl alcohol possess extremely acrid, irritating odors and are potent lachrimators! They are also toxic. Always work with with gloves and safety glasses. Chromium trioxide is a potent oxidizer, also wear latex gloves and avoid exposure to organic matter. Propargyl alcohol and chromium trioxide are cancer suspect agents. 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 many days with no apparent significant decomposition

Data

B.p. 54-58° (760mm) , n_D25 1.4050
A 2,4-dinitrophenylhydrazone was prepared by the Shriner and Fuson procedure.
See other reference 1. Recrystallization from ethanol yielded yellow crystals, m.p. 121.-113^0 (lit.: m.p. 1.22.5-127.5°), See other reference 2.

Lead Reference

J. C. Sauer, "Organic Syntheses", Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N.Y.,1963, p. 813. Org. Synth. 1956, 36,56
http://www.orgsyn.org/Content/pdfs/procedures/CV4P0813.pdf

Other References

1) L. Shriner, R. C. Fuson, and D. Y. Curtin,"The Systematic Identification of Organic Compounds", 5th ed., John Wiley and Sons, Inc., New York, N. Y., 1964.

2) "Tables for Identification of Organic Compounds", compiled by M. Frankel and S. Patai, The Chemical Rubber Co., Cleveland, Ohio, 1960.

Keywords: alcohols, **aldehydes**, **alkynes**, **oxidation**