J. Chem. Research (S),
1997, 207†

A Short, Convenient Synthesis of Propynal†

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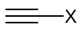
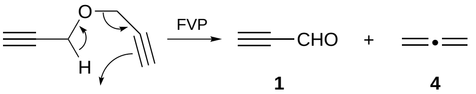
Propynal **1** is obtained in 80% yield on a preparative scale by flash vacuum pyrolysis of diprop-2-ynyl ether **3**.

Propynal (propargyl aldehyde) **1** is a useful three-carbon reagent which can be made on a large scale by an *Organic Syntheses* route involving chromium trioxide oxidation of prop-2-ynyl alcohol **2**.[1] However, this is a low-yielding method (35–41%) with inconvenient work-up due in part to the low boiling point (54–57 °C) of the product. The procedure is particularly awkward if only a small quantity of propynal **1** is required. A more recent variant may be useful for producing a solution of the aldehyde,[2] but in our hands[3] it proved impossible to separate the product from the mixture of solvents employed, using standard laboratory distillation apparatus. Here we report full experimental conditions for a convenient one-step flash vacuum pyrolysis (FVP) route to pure propynal **1** based on the retro-ene reaction of commercially available diprop-2-ynyl ether **3** (Scheme 1).[4] This reaction has been studied previously, but details are not readily available.[5,6] An analogous procedure has been used to generate propynethial from diprop-2-ynyl sulfide for *in situ* photoelectron spectroscopic determination.[7] The participation of prop-2-ynyl groups in retro-ene reactions has been widely investigated kinetically[6,8,9] and shown to be concerted[10] and consistently faster than the reaction of the corresponding allyl derivative.[6] FVP of silylated prop-2-ynyl ethers has been used as a preparative route to silylallenes.[11]



1 X = CHO
2 X = CH_2OH



3 **1** **4**

Scheme 1

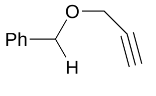
Small-scale (*ca*. 100 mg) pyrolyses of diprop-2-ynyl ether **3** were successful at 750 °C, generating essentially quantitative yields of propynal **1** [δ_H 9.16 (1 H, s) and 3.51 (1 H, s)] under these conditions. Significant amounts of starting material were recovered at lower pyrolysis temperatures. Allene **4**, the only co-product, was identified by its characteristic singlet at δ_H 4.62 in the ^1H NMR spectrum of the crude pyrolysate.

Owing to the volatility of both the precursor and the product, minor design modifications for both the inlet and the trap systems of our standard FVP apparatus were required for successful pyrolyses on a preparative (*ca*. 2 g) scale (see Experimental section). It is particularly important to ensure that the volatile products do not block the trap, since this leads to an increase in contact time of the precursor in the furnace and causes the formation of a brown polymeric deposit at the exit point. After completion of the pyrolysis, the majority of the allene (bp −34 °C) evaporates when the trap is allowed to warm to room temperature under an atmosphere of nitrogen. The mobile liquid residue is almost pure propynal **1**, and reproducible yields of 80% can be routinely achieved.

Gas-phase thermolysis of unsymmetrical prop-2-ynyl ethers to give carbonyl compounds may have more general application in synthesis, and as a simple example we have obtained benzaldehyde **5** (63%) by FVP of benzyl prop-2-ynyl ether[8,12] **6** at 750 °C (0.1 Torr).

PhCHO

5



6

Experimental

^1H NMR spectra were recorded at 200 MHz for solutions in [^2H]chloroform.

Propynal (**1**).—Diprop-2-ynyl ether[4] **3** (2.0 g, 21 mmol) was weighed into a round-bottomed flask and connected *via* a right-angled adaptor to an empty silica furnace tube (35 × 2.5 cm) which was maintained at 750 °C by an electrically heated furnace. The exit end of the furnace tube was connected to a U-tube trap of 1.9 cm internal diameter, which was cooled in liquid nitrogen. The inlet flask was cooled in ice, and the whole system was evacuated to a pressure of 10^{-2}–10^{-3} Torr. The ether distilled through the furnace as the ice melted over a period of 40–60 min. If necessary the evaporation was completed by warming the flask in warm (*ca*. 60 °C) water. If the products blocked the trap, the liquid nitrogen level at the trap was lowered as soon as possible by 1–2 cm to allow the products to melt, flow down the tube and resolidify. The product which remained in the trap after it warmed to room temperature was almost pure propynal **1** (0.92 g, 80%), δ_H 9.16 (1 H, s) and 3.51 (1 H, s); *m*/*z* 54 (33%) and 53 (100), which was sufficiently pure for most synthetic purposes.

Benzaldehyde (**5**).—Benzyl prop-2-ynyl ether[12] **6** (0.5 g, 4.7 mmol) was distilled at 10^{-1} Torr under similar conditions to those described above, into the furnace which was maintained at 750 °C. The sole product in the trap after evaporation of allene was benzaldehyde (0.23 g, 63%), δ_H 10.02 (1 H, s), 7.88 (2 H, m) and 7.45–7.65 (3 H, m).

Received, 20th January 1997; Accepted, 17th March 1997
Paper E/7/00453B

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