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Condensation of Prop-2-ynyl Alcohols with 2-Alkylalk-2-enals. A Simple Synthesis of Allenic Aldehydes

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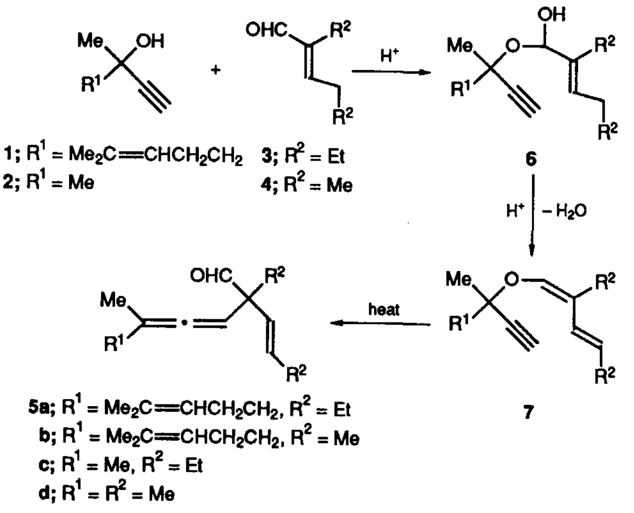
The acid-catalysed condensation of tertiary prop-2-ynyl alcohols with 2-alkylalk-2-enals gave allenic aldehydes **5a–d**.

The acid-catalysed condensation of prop-2-ynyl alcohols with isobutyraldehyde is known to give 2,2-dimethylalka-3,4-dienals.[1–3] A novel example demonstrating the synthetic utility of this reaction has been given in our recent publication[4] dealing with the transformation of dehydrolinalool **1** into 2,2,5,9-tetramethyldeca-3,4,8-trienal, which readily underwent further conversion into cyclopentene derivatives. Unbranched saturated aldehydes such as butanal condense with dehydrolinalool to give mixtures of products.[5]

It was of interest whether or not the condensation would proceed with aldehydes having no enolisable hydrogen on C-2. In order to answer this question we performed a condensation of dehydrolinalool **1** and 2-methylbut-3-yn-2-ol **2** with 2-alkylalk-2-enals **3** and **4**. This reaction resulted in the formation of the allenic aldehydes **5a–d** as the sole products in isolable yields of 62% (**5a**), 62% (**5b**), 64% (**5c**) and 55% (**5d**) (Scheme 1).†



Scheme 1

The formation of **5a–d** aldehydes appears to be caused by the migration of a double bond during the dehydration of an intermediate hemiacetal **6** to give the ether **7** (Scheme 1).

In a typical reaction, a solution of 0.2 mol of prop-2-ynyl

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† All new compounds gave satisfactory spectroscopic and analytical data. Selected ^{1}H NMR (250 MHz, $CDCl_3$, standard $SiMe_4$) and ^{13}C NMR (62.9 MHz, C_6D_6, standard $SiMe_4$) data for **5a**: two diastereoisomers (~ 1:1), δ_H 9.29 (1H, s, CHO), 5.64 and 5.36 (1H and 1H, 2m; HC=CH), 5.11 (1H, m, 8-H), 5.03 (1H, m, 3-H), 2.09 and 1.97 (4H and 2H, 2m, 3 CH_2C=), 1.71 and 1.70 (3H, 2d, *J* 2.9 Hz, 5-Me), 1.68 (2H, m, 2-CH_2), 1.67 and 1.59 (3H and 3H, 2m, Me_2C=), 0.99 (3H, t, *J* 7.5 Hz, CH_3CH_2), 0.87 and 0.86 (3H, 2t, *J* 7.5 Hz, CH_3CH_2); δ_C 203.0 and 202.9, 198.9 and 198.8, 135.8 and 135.7, 131.7, 128.7 and 128.6, 124.5 and 124.4, 102.6, 91.7 and 91.6, 57.0, 36.4, 28.1 and 27.9, 26.7, 26.3, 25.7, 19.1 and 19.0, 17.7, 13.8, 8.9 and 8.8.

For **5b**: two diastereoisomers (~ 1:1), δ_H 9.31 and 9.30 (1H, 2s, CHO), 5.61 and 5.46 (1H and 1H, 2m, HC=CH), 5.10 (1H, m, 8-H), 5.07 (1H, m, 3-H), 2.07 and 1.96 (2H and 2H, 2m, CH_2CH_2), 1.73 (3H, dd, *J* 6.0, 1.3 Hz, CH_3CH=), 1.71 and 1.70 (3H, 2d, *J* 2.9 Hz, 5-Me), 1.67 and 1.59 (3H and 3H, 2m, Me_2C=), 1.21 (3H, s, 2-Me); δ_C 202.1, 198.7 and 198.6, 132.2, 131.7, 127.5 and 127.4, 124.5, 103.1, 93.3, 53.0 and 52.9, 34.4 and 34.3, 26.6, 25.7, 20.2, 19.1, 18.3, 17.7.

For **5c**: δ_H 9.72 (1H, s, CHO), 5.63 and 5.34 (1H and 1H, 2dt, *J* 15.8, 6.3 and 15.8, 1.5 Hz, HC=CH), 4.95 (1H, sept, *J* 2.9 Hz, 3-H), 2.09 (2H, m, CH_2C=), 1.71 and 1.69 (3H and 3H, 2d, *J* 2.9 Hz, Me_2C=), 1.68 (2H, m, 2-CH_2), 0.99 and 0.86 (3H and 3H, 2t, *J* 7.4 Hz, 2 CH_3CH_2); δ_C 203.4, 198.8, 135.8, 128.6, 98.1, 90.1, 57.1, 27.9, 26.3, 20.4, 20.3, 13.8, 8.9.

For **5d**: δ_H 9.29 (1H, s, CHO), 5.61 and 5.45 (1H and 1H, 2dq, *J* 15.7, 6.2 and 15.7, 1.4 Hz, HC=CH), 4.99 (1H, sept, *J* 2.9 Hz, 3-H), 1.73 (3H, dd, *J* 6.2, 1.4 Hz, CH_3CH=), 1.71 and 1.70 (3H and 3H, 2d, *J* 2.9 Hz, Me_2C=), 1.20 (3H, s, 2-Me); δ_C 202.6, 198.4, 132.0, 127.5, 98.6, 91.8, 53.0, 20.4, 20.4, 20.1, 18.3.

alcohol **1**, **2**, 0.6 mol of aldehyde **3**, **4** and 0.6 mmol of sulphosalicylic acid (3-carboxy-4-hydroxybenzenesulphonic acid) in 120 ml of toluene was refluxed for 7 h, the water formed being collected in a Dean–Stark separator. After neutralization the reaction mixture was distilled under vacuum to give 2-alkyl-2-(1-alkynyl)alka-3,4-dienals **5a–d**.

The allenic aldehydes **5a–d** possess interesting odours and may find a use as new fragrances.

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