Short Communication

An Intramolecular Addition of a Hemiacetal Hydroxy Group to an Allene

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In connection with our interest in the synthesis of pheromones containing cyclobutane rings, large quantities of the allenic aldehydes 1 were needed. All three aldehydes are readily obtainable in low to moderate yields (35–54%) from isobutyraldehyde and the appropriate propargylic alcohol via a Claisen-Cope type rearrangement (Scheme 1). For all three aldehydes 1a–c, simple distillation left a significant amount of residual tars, viz. 40, 20 and 15% by weight, respectively. According to GLC analyses the distillates consisted of complex mixtures of which the allenic aldehydes 1 constituted the major components. In the distillate containing 1c a second major component was present; the ratio between this compound and 1c was 1:3.8, and they were separated by fractional distillation. The former was isolated as a white, crystalline compound and identified as the dihydropyran 2c on the basis of spectroscopic evidence. The molecular weight was found from chemical ionisation MS to be 222. An IR absorption band at 3300 cm⁻¹ indicated a terminal alkyne. Surprisingly, no absorption due to the C≡C stretching vibration was observed, but the NMR spectra were in accord with the proposed structure. In the ¹³C NMR spectrum the two alkyne carbons appear with ¹JCH = 249 Hz and ²JCH = 49 Hz, which are nearly identical with those found for acetylene itself. The ¹H NMR shifts correspond well to those of the analogues carbocycle 2,4-hydroxy-3,3,6,6-tetramethylcyclohex-4-enone, reported recently. Chemical evidence for the acetal nature of the compound was obtained from the fast and quantitative conversion of 2c to compounds 2d and 2e in the presence of an excess of methanol and 2-propanol, respectively.

The most likely pathway for the formation of 2c seems to be via 1c, as depicted in Scheme 2. The mechanism is supported by reports in the literature that both phenolic and alcholic hydroxy groups can add intramolecularly to an allene under acidic conditions. Further evidence for our mechanistic proposal was obtained from the reaction of the aldehyde 1c with an excess of methanol or 2-propanol in the presence of a catalytic amount of HgSO₄; heating under reflux for 4–6 h resulted in quantitative yields of 2d and 2e, respectively. Applying the same reaction conditions to the aldehydes 1a and 1b, mixtures of
products resulted in which no single component constituted more than 30% as indicated by GLC. On the other hand, treatment of 1c with 2-methyl-3-butyn-2-ol, methanol or 2-propanol in the presence of p-toluenesulfonic acid under reflux afforded mixtures of compounds containing 2c, 2d and 2e, respectively, as major products. The reactions were very slow, requiring more than 100 h for completion. Similar reactions with the aldehydes 1a and 1b resulted in complex mixtures which were not investigated further.

The formation of 2c as a by-product seems unavoidable under the reaction conditions employed for the preparation of 1c, though the yield of the former is favoured by long reaction times. The formation of 2c is a novel example of an intramolecular addition to the allenic linkage, a reaction well documented for allenic alcohols.\footnote{12}

General for the syntheses of the allenic aldehydes 1. The reactions were carried out as described in the literature,\footnote{2,4-7} starting with 1.0–1.5 mol of isobutyraldehyde and 1.0 mol of the appropriate propargylic alcohol. Simple distillation of the resulting reaction mixture separated it into a volatile fraction and a tarry residue. The volatile material was analyzed by GLC and the amount of 1 is reported as per cent of the volatiles corrected for solvent and unreacted starting materials. The amount of residue is reported as weight % based on the weight of the starting materials.

Reaction of isobutyraldehyde and 2-propynol. The aldehyde 1a was isolated as the only major compound in 42% yield; the remaining material consisted of a complex mixture of compounds.

Reaction of isobutyraldehyde and 3-butyn-2-ol. The aldehyde was isolated in 56% yield as the only major volatile compound.

Reaction of isobutyraldehyde and 2-methyl-3-butyn-2-ol. In the volatile fraction, compounds 1c and 2c were present in a ratio of 3.8:1. Fractional distillation gave 1c and 2c in 50 and 13% yields, respectively. The white, crystalline compound 2c was further purified by sublimation (60°C/10 mmHg).
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3,6-Dihydro-2-(1,1-dimethyl-2-propynoxy)-3,3,6,6-tetramethyl-2H-pyran (2e). M.p. 59–60°C, b.p. 102–104°C/30 mmHg. MS[(Cl, CH₃); m/z]: 223 (M+1), 139 (M⁺–C₃H₅O, 100 %). MS[IP 70 eV; m/z (% rel. int.):] 207 (0.8), 139 (10), 110(100), 95(66), 67(26), 55(13), 43(40), 41 (36), 39(17). IR (CCl₄): 3300 (m), 3060 (w), 2970(m), 2930 (m), 2900 (w), 2865 (m), 1465 (m), 1370(m), 1360 (m) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 0.97 (s, 3H), 0.99 (s, 3H), 1.29 (s, 3H), 1.32 (s, 3H), 1.52 (s, 3H), 1.58 (s, 3H), 2.41 (s, 1H), 4.96 (s, 1H), 5.39 (d, J = 10.8 Hz, 1H), 5.41 (d, J = 10.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 21.3 (CH₃), 24.9 (CH₃), 26.2 (CH₃), 29.5 (CH₃), 29.9 (CH₃), 30.5 (CH₃), 35.7 (c), 71.6 (O–C), 72.1 (≈C–H, JCH = 249 Hz), 74.9 (O–C), 86.8 (≈C, JCH = 49 Hz), 98.0 (O–CH=O, JCH = 156 Hz), 131.9 (=CH), 133.3 (=CH).

Exchange reaction of 2e with alcohols. Solutions of 2e (1.00 g, 4.5 mmol) in methanol or 2-propanol (20 ml) with catalytic amounts of p-toluenesulfonic acid were heated under reflux for 10 min or 1 h to give complete conversion to 2d and 2e, respectively.

3,6-Dihydro-2-methoxy-3,3,6,6-tetramethyl-2H-pyran (2d). ¹H NMR (300 MHz, CDCl₃): δ 0.97 (s, 6H), 1.28 (s, 3H), 1.29 (s, 3H), 3.46 (s, 3H), 4.29(s, 1H), 5.36 (d, J = 10.0 Hz, 1H), 5.45 (d, J = 10.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 21.5 (CH₃), 25.3 (CH₃), 26.7 (CH₃), 29.6 (CH₃), 35.5 (C), 56.2 (CH₂O), 73.8 (O–C), 103.8 (O–CH=O), 131.7 (=CH), 132.3 (=CH).

3,6-Dihydro-2-(1-methylethoxy)-3,3,6,6-tetramethyl-2H-pyran (2e). MS[Cl, CH₃]; m/z]: 199 (M+1), 139 (M⁺–C₃H₅O, 100 %). MS[IP 70 eV; m/z (% rel. int.):] 197(0.1), 111(15), 110(100), 95 (98), 81(10), 69(10), 67(16), 55(17), 43(51), 41 (35), 39(12). ¹H NMR (300 MHz, CDCl₃): δ 0.94 (s, 3H), 0.98 (s, 3H), 1.14 (d, J = 6.1 Hz, 3H), 1.24 (d, J = 6.1 Hz, 3H) 1.28 (s, 3H), 1.29 (s, 3H), 3.92 (heptet, J = 6.1 Hz, 1H), 4.47 (s, 3H), 5.37 (d, J = 10.0 Hz, 1H), 5.43 (d, J = 10.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 21.3 (CH₃), 21.7 (CH₃), 23.3 (CH₃), 25.0 (CH₃), 26.4 (CH₃), 29.8 (CH₃), 35.4 (C), 69.8 (O–CH), 7.39 (O–C), 99.9 (O–CH=O), 131.8 (=CH), 132.8 (=CH).

Synthesis of 2e catalyzed by HgSO₄. Mixtures of 1e (1.00 g, 7.2 mmol), methanol or 2-propanol (20 ml) and HgSO₄ (150 mg, 0.51 mmol) were heated under reflux for 4–6 h to give quantitative yields of 2d and 2e, respectively.

Reaction of 1e with alcohols. Solutions of 1e (1.00 g, 7.2 mmol) and a catalytic amount of p-toluenesulfonic acid in either 2-methyl-3-butyn-2-ol, methanol or 2-propanol (20 ml) were heated under reflux for ~100 h. The reactions were monitored by GLC. Neutralization with Na₂CO₃, drying (MgSO₄) and evaporation followed by short-path distillation gave 2e, 2d and 2e, respectively, in 50–60 % yields.

References

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