Short Communication

An Intramolecular Addition of a Hemiacetal Hydroxy Group to an Allene

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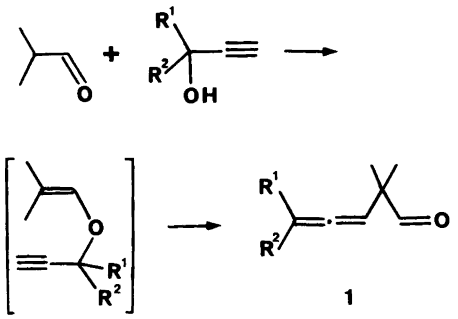
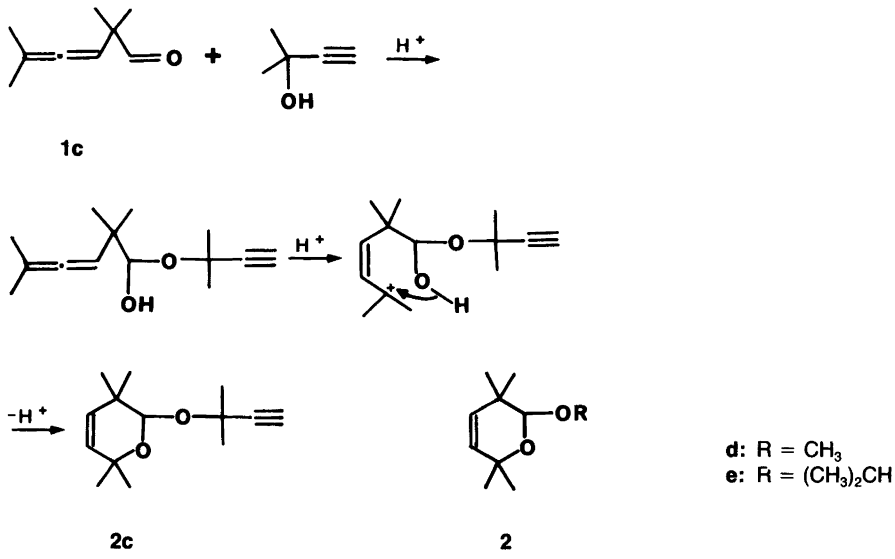
In connection with our interest in the synthesis of pheromones containing cyclobutane rings,[1–3] large quantities of the allenic aldehydes **1** were needed. All three aldehydes are readily obtainable [2,4–7] in low to moderate yields (35–54 %) from isobutyraldehyde and the appropriate propargylic alcohol 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 ^{13}C NMR spectrum the two alkyne carbons appear with $^1J_{CH}$ = 249 Hz and $^2J_{CH}$ = 49 Hz, which are nearly identical with those found for acetylene itself.[8] The ^1H NMR shifts correspond well to those of the analogues carbocycle 2-hydroxy-3,3,6,6-tetramethylcyclohex-4-enone, reported recently.[9] 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.



Scheme 1.

a: $R^1 = R^2 = H$
b: $R^1 = H$; $R^2 = CH_3$
c: $R^1 = R^2 = CH_3$

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[10] and alcoholic[11] 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 $HgSO_4$; 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



Scheme 2.

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.[12]

Experimental

General. GLC analyses were performed using a 25 m capillary SP 2100 SCOT column. IR spectra were recorded on a Perkin-Elmer 1310 instrument. Routine ^{1}H NMR spectra were recorded on a Varian EM 360 A instrument, high-field NMR spectra on a Varian XL-300 instrument and MS spectra ona GLC/MS VG micromass 7070F.

General for the syntheses of the allenic aldehydes **1**. The reactions were carried out as described in the literature,[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).

3,6-Dihydro-2-(1,1-dimethyl-2-propynoxy)-3,3,6,6-tetramethyl-2H-pyran (**2c**). M.p. 59–60 °C, b.p. 102–104 °C/30 mmHg. MS[(CI, CH_4); *m/z*]: 223 (M+1), 139 ($M^+-C_5H_7O$, 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 (CCl_4): 3300 (m), 3060 (w), 2970(m), 2930 (m), 2900 (w), 2865 (m), 1465 (m), 1370(m), 1360 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 24.9 (CH_3), 26.2 (CH_3), 29.5 (CH_3), 29.9 (CH_3), 30.5 (CH_3), 35.7 (c), 71.6 (O–C), 72.1 (≡C–H, $^1J_{CH}$ = 249 Hz), 74.9 (O–C), 86.8 (≡C, $^2J_{CH}$ = 49 Hz), 98.0 (O–CH–O, $^1J_{CH}$ = 156 Hz), 131.9 (=CH), 133.3 (=CH).

Exchange reaction of **2c** *with alcohols.* Solutions of **2c** (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), $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5 (CH_3), 25.3 (CH_3), 26.7 (CH_3), 29.6 (CH_3), 35.5 (C), 56.2 (CH_3O), 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[CI, CH_4); *m/z*]: 199 (M+1), 139 ($M^+-C_3H_7O$, 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, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3 (CH_3), 21.7 (CH_3), 23.3 (CH_3), 25.0 (CH_3), 26.4 (CH_3), 29.8 (CH_3), 35.4 (C), 69.8 (O–CH), 7.39 (O–C), 99.9 (O–CH–O), 131.8 (=CH), 132.8 (=CH).

Synthesis of **2c** *catalyzed by* $HgSO_4$. Mixtures of **1c** (1.00 g, 7.2 mmol), methanol or 2-propanol (20 ml) and $HgSO_4$ (150 mg, 0.51 mmol) were heated under reflux for 4–6 h to give quantitative yields of **2d** and **2e**, respectively.

Reaction of **1c** *with alcohols.* Solutions of **1c** (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 Na_2CO_3, drying ($MgSO_4$) and evaporation followed by short-path distillation gave **2c**, **2d** and **2e**, respectively, in 50–60 % yields.

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