Synthesis of *Z*-11-octadecenal, the sex pheromone of the wax moth

N. Ya. Grigor'eva, P. G. Tsiklauri, and A. V. Buevich*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

A new synthesis of *Z*-11-octadecenal, the sex pheromone of the wax moth *Achroia grisella* starting from methyl 10-undecenoate is elaborated.

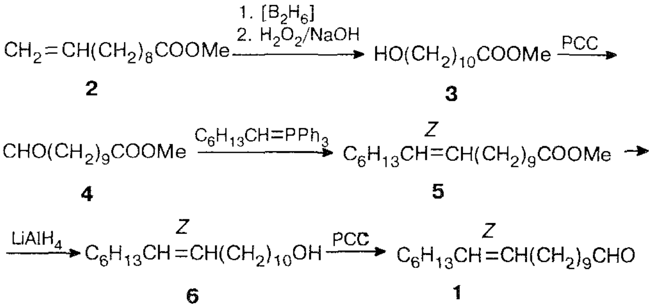
Key words: insect pheromone, stereoselective synthesis; Wittig reaction; hydroboration.

Z-11-Octadecenal (**1**), the sex feromone of the wax moth *Achroia grisella* (a specific pest of the honey bee[1] and a minor component of the pheromone blend of the cotton-stem *Earias vitella*),[2] has been synthesized before starting from acetylenic compounds.[3,4] Here we describe a synthesis of **1** from methyl undecenoate (**2**) using Bestmann's variant of the Wittig reaction as the key stage of constructing the *Z*-olefinic bond.

The hydroboration-oxidation of **2** with tetrapropyldiborane or diborane does not affect the ester group and affords the hydroxyester **3** in a high yield. The application of diborane generated from $NaBH_4$ by treatment with dimethyl sulfate is particularly suitable for large-scale hydroboration of **2**.[6] The condensation of aldehyde **4**, obtained by oxidizing **3** with pyridinium chlorochromate (PCC), with heptylidenetriphenylphosphorane (generated from the corresponding phosphonium salt using $(Me_3Si)_2NNa$[5]) affords the known ester **5** in a preparative yield. The *Z*-configuration of ester **5** was unequivocally confirmed by the value of the spin coupling constant $^3J_{CH=CH}$ = 11.2 Hz (determined from the analysis of the ^1H NMR spectrum of the vinyl protons' ^{13}C-satellites).

The hydride reduction of **5** and the oxidation of alcohol **6** thus formed with PCC complete the synthesis of the target compound **1**.

Scheme 1



$$CH_2=CH(CH_2)_8COOMe \xrightarrow[2.\ H_2O_2/NaOH]{1.\ [B_2H_6]} HO(CH_2)_{10}COOMe \xrightarrow{PCC}$$

2 **3**

$$CHO(CH_2)_9COOMe \xrightarrow{C_6H_{13}CH=PPh_3} \overset{Z}{C_6H_{13}CH=CH(CH_2)_9COOMe} \rightarrow$$

4 **5**

$$\xrightarrow{LiAlH_4} \overset{Z}{C_6H_{13}CH=CH(CH_2)_{10}OH} \xrightarrow{PCC} \overset{Z}{C_6H_{13}CH=CH(CH_2)_9CHO}$$

6 **1**

Experimental

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in CCl_4. ^1H NMR spectra were registered on a Bruker WM-250 instrument in $CDCl_3$ with TMS as the standard, ^{13}C NMR spectra were taken on a Bruker AM-300 spectrometer at 75.5 Hz. The preparative flash chromatography was performed on silica gel L (40—100 μm, Chemapol, CzSFR), and thin layer chromatography was carried out using Silufol plates (Kavalier, CzSFR) in a 1:1 ether/hexane mixture as the eluent.

11-Hydroxyundecanoic acid methyl ester (3). A. A solution of tetrapropyldiborane (0.53 g, 2.74 mmol) in 2 mL of THF was added dropwise with stirring at 0 °C to a solution of methyl 11-undecenoate (**2**) (1 g, 5 mmol) in 10 mL of THF and the mixture was stirred for 30 min at 0 °C. Then it was warmed up to ~20 °C in 2 h, and 1 mL of MeOH was added. The reaction mixture was cooled down again to −5 °C, and 1.6 mL of 3*N* NaOH and 1.6 mL of 30 % H_2O_2 were added dropwise in successsion. After the usual workup an oily product (1.7 g) was column chromatographed through 50 g of silica gel by gradient elution (from 100 % hexane to 100 % ether) to afford 0.97 g (89 %) of **3** with physicochemical characteristics consistent with those reported earlier.[7] ^1H NMR, δ: 1.28 (m, 14 H, CH_2); 1.58 (m, 2 H, CH_2); 2.3 (t, 2 H, CH_2(2), J = 7.5 Hz); 3.63 (t, 2 H, CH_2O, J = 7 Hz); 3.66 (s, 3 H, CH_3).

B. A solution of 0.75 g (6 mmol) of dimethyl sulfate in 2 mL of THF (dropwise; 5 min) and a solution of 2.5 g (12.5 mmol) of **2** in 2.5 mL of THF were added successively at 30 min intervals to a stirred suspension of $NaBH_4$ (0.28 g, 6 mmol) in 7 mL of THF maintained at 0 °C under Ar. The reaction mixture was stirred until complete dissappearance of **2** (TLC monitoring) and then was worked up as above. The yield of chromatographically pure **3** was 78 %.

Methyl 11-oxoundecanoate (4) was obtained by oxidizing alcohol **3** with PCC in CH_2Cl_2 in the presence of CH_3COONa following the standard procedure. Purification using chromatography through silica gel with a gradient elution from 100 % hexane to 15 % ether/hexane furnished aldehyde **4** in 55 % yield with physicochemical characteristics consistent with earlier data.[8] ^1H NMR, δ: 1.29 (br. s, 10 H, CH_2); 1.6 (m, 4 H, CH_2); 2.3 (t, 2 H, CH_2(2), J = 7.5 Hz); 2.41 (dt, 2 H, CH_2(10), J_1 = 2 Hz, J_2 = 7.5 Hz); 3.67 (s, 3 H, CH_3); 9.75 (t, 1 H, CHO, J = 2 Hz).

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Methyl *Z*-11-octadecenoate (5). A solution of heptyltriphenylphosphonium bromide (4.68 g, 10.6 mmol) in 10 mL of THF was added under Ar to a stirred solution of $(Me_3Si)_2NNa$ (12 mmol), freshly prepared from Na (0.28 g, 12 mg-at), $(Me_3Si)_2NH$ (1.58 g, 12 mmol), and phenantrene (1.07 g, 6 mmol) in 15 mL of THF after the known method.[9] The reaction mixture was stirred for 30 min at room temperature and then refluxed for 1 h. The bright orange solution thus obtained was cooled to −78 °C, and **4** (1.52 g, 7.1 mmol) was added dropwise. Then the temperature was raised gradually to ~20 °C, and the mixture was stirred for 2 additional hours and left overnight. A saturated solution of NH_4Cl was then added (with stirring) to the reaction mixture cooled to 0 °C. The usual workup afforded 2.34 g of a light yellow oil, which was subjected to column chromatography through 150 g of silica gel. A gradient of 100 % hexane to 100 % ether was used to give 1.26 g (60 %) of **5** with physicochemical characteristics consistent with those of the literature.[10] ^1H NMR, δ: 0.9 (t, 3 H, CH_3, J = 6.8 Hz); 1.3 (m, 20 H, CH_2); 1.63 (m, 2 H, CH_2); 2.03 (m, 4 H, $CH_2C{=}C$); 2.3 (t, 2 H, CH_2(2), J = 7,5 Hz); 3.67 (s, 3 H, CH_3O); 5.35 (m, 2 H, HC=CH).

***Z*-11-Octadecenol (6)** was obtained conventionally by reduction of **5** with $LiAlH_4$ in ether. Column chromatography through silica gel with a gradient elution from 100 % hexane to 40 % ether/hexane yielded alcohol **6** (94 %), whose physicochemical characteristics were consistent with those reported earlier.[4] ^1H NMR, δ: 0.89 (t, 3 H, CH_3, J = 6.5 Hz); 1.3 (m, 22 H, CH_2); 1.58 (m, 2 H, CH_2); 2.02 (m, 4 H, $CH_2C{=}C$); 3.67 (t, 2 H, CH_2O, J = 7 Hz); 5.35 (m, 2 H, HC=CH). ^{13}C NMR, δ: 14.08 (CH_3), 22.64, 25.72, 27.19, 28.97, 29.28, 29.42, 29.52, 29.55, 29.58, 29.73 (CH_2), 31.77, 32.72 ($\underline{C}H_2C{=}C$), 63.06 (CH_2O), 129.85, 129.89 (CH=CH).

***Z*-11-Octadecenal (1)** was obtained by oxidizing **6** with PCC as described above for **4**. Chromatographic purification afforded **1** in 61 % yield. The physicochemical characteristics of the specimen were in agreement with those of the literature.[3,4] ^1H NMR, δ: 0.9 (t, 3 H, CH_3, J = 6.5 Hz); 1.3 (m, 20 H, CH_2); 1.63 (m, 2 H, CH_2); 2.02 (m, 4 H, $CH_2C{=}C$); 2.42 (dt, 2 H, $C\underline{H_2}CHO$, J_1 = 2 Hz, J_2 = 7.5 Hz); 5.35 (m, 2 H, HC=CH); 9.78 (t, 1 H, CHO, J = 2 Hz).

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