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SYNTHESIS OF (*Z*/*E*)-11-TETRADECEN-1-OL, A COMPONENT OF *Ostrinia nubilalis* SEX PHEROMONE

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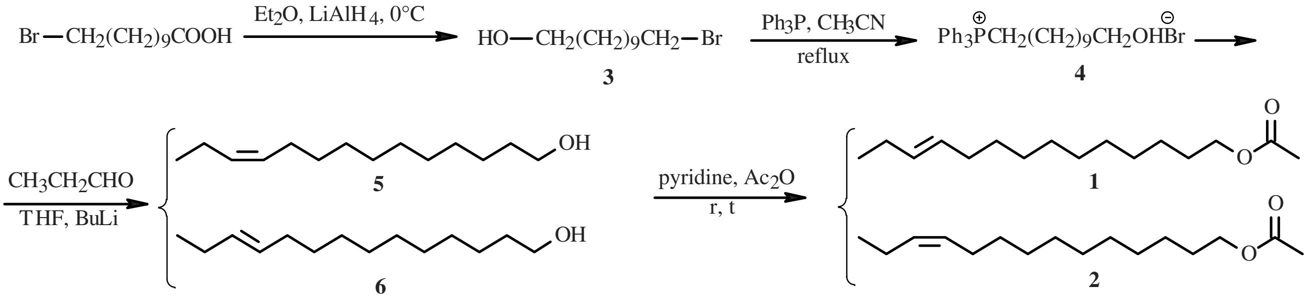
11-Tetradecen-1-ol acetate is a mixture of geometric isomers with the Z/E*-conformations in a 94:6 ratio that is used as an attractant to trap corn pests. It has a powerful attractive action similar to that of an isomeric mixture of 11-tetradecenyl acetate with the* Z/E*-conformation in a 95:5 ratio that was extracted from the peritoneal cavity of male* Ostrinia nubilalis *Hubner in Xinjing (PRC).*

Key words: *Ostrinia nubilalis* Hubner, sex pheromone, (*Z*/*E*)-11-tetradecen-1-ol acetate, synthesis.

Herein we report a cheaper and simpler synthetic method for 11-tetradecen-1-ol acetate in 34.8% overall yield. The European corn borer (*Ostrinia nubilalis* Hubner) is a common pest that is widely distributed in Europe and the Far East and decreases grain production. The goal of our work was to find a suitable agent for controlling corn pests. For this reason, we synthesized the sex pheromone of the European corn borer.

Several synthetic methods for the sex pheromone of the Asian corn borer have been reported [1-4]. However, little information is available on the synthesis of pheromones of the European corn borer [5-6]. The reported methods produced pheromones in low yields from expensive reagents. Thus, the goal of our work was to find an economical and convenient synthetic method for the sex pheromones of *O. nubilalis* Hubner.

We report the synthesis of the sex pheromone of the European corn borer (**1** and **2**) in 34.8% overall yield. The starting compound was a cheap 11-undecanoic acid, reduction of which with $LiAlH_4$ produced bromhydrin **3**. Then, reaction of **3** with triphenylphosphine gave (11-hydroxyundecyl)triphenylphosphonium bromide **4**. A double bond was constructed using a Wittig reaction. Propionaldehyde and (11-hydroxyundecyl)triphenylphosphonium bromide reacted to give a mixture of geometric isomers (*Z*/*E*)-11-tetradecen-1-ols **5** and **6**, acetylation of which gave the *Z*-isomer with an impurity of the *E*-isomer (94:6 ratio).



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EXPERIMENTAL

IR spectra were recorded on a Perkin—Elmer 983 spectrophotometer; PMR spectra, on a Varian Inova-400 spectrometer (TMS internal standard, $CDCl_3$ solvent). Melting points were determined on an XT-4 instrument and are uncorrected. Commercially available reagents were used without further purification. Dichloromethane, ether, and pyridine were freshly distilled. THF was distilled over sodium and benzophenone before use.

Synthesis of 11-Bromoundecan-1-ol (3). A three-necked flask (250 mL) was charged with $LiAlH_4$ (3.416 g, 0.09 mol) and anhydrous ether (35 mL). The mixture was stirred under N_2 for 30 min at -10°C [7], cooled below -10°C, treated dropwise with 11-bromoundecanoic acid (19.89 g, 0.075 mol) in absolute ether (145 mL) under N_2 and then at room temperature for 30 min, refluxed for 1 h, cooled to room temperature, and treated with aqueous NaOH solution (15 mL, 5%) until the gray precipitate turned white. The precipitate was filtered off and washed with ether (3 × 10 mL). The organic layers were combined and dried over $MgSO_4$. Ether was removed to produce a white solid that was crystallized repeatedly from ethanol to afford **3** (16.5 g). Colorless crystals, 81.4% yield, mp 43-46°C. IR spectrum (ν_{max}, cm^{-1}): 3429, 2923, 2852, 1466, 1057, 725, 645.

PMR spectrum (δ, ppm, J/Hz): 3.58 (2H, t, J = 6, CH_2OH), 3.37 (2H, t, J = 6.3, $BrCH_2$), 2.50-2.51 (1H, s, OH), 1.76-1.81 (2H, m, 10-CH_2), 1.35-1.41 (2H, m, 2-CH_2), 1.25 (12H, m, 6CH_2).

Synthesis of (11-Hydroxyundecyl)triphenylphosphonium Bromide (4). Compound **3** (16.00 g, 0.064 mol), triphenylphosphine (19.67 g, 0.075 mol), and CH_3CN (265 mL) were stirred in a three-necked round-bottomed flask (500 mL) equipped with a reflux condenser for 24 h [8]. The solvent was replaced by ether (80 mL). The mixture was stirred at room temperature. A white precipitate quickly formed and was filtered off and washed with ether three times. Solvent was removed to afford **4** (28.4 g). White solid, 87.4% yield, mp 89-92°C. IR spectrum (ν_{max}, cm^{-1}): 3273, 3016, 2924, 2853, 1437, 1113, 1106, 1059, 749, 692.

PMR spectrum (δ, ppm, J/Hz): 7.69-7.87 (15H, m, 3C_6H_5), 3.77 (2H, t, J = 8, CH_2O), 2.17 (1H, s, OH), 1.52-1.63 (2H, m, 2-CH_2), 1.29-1.32 (2H, m, 11-CH_2), 1.20-1.25 (14H, m, 7CH_2).

Synthesis of (*Z/E*)-11-Tetradecen-1-ols 5 and 6. A suspension of **4** (28.0 g, 0.055 mol) in dry THF (150 mL) was treated with *n*-butyllithium in hexane (2.5 M, 24 mL, 0.060 mol). The mixture was stirred at -15°C under N_2 for 2 h [9, 10], treated dropwise with propionaldehyde (3.77 g, 0.065 mol) in dry THF (10 mL), stirred at -15°C for 2 h and overnight at room temperature, treated with saturated NH_4Cl solution (20 mL), stirred for 30 min, and filtered. The organic layer was washed successively with water and saturated NaCl solution, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The product was purified by flash chromatography over a column of silica gel (100-200 mesh) with elution by petroleum ether-ethylacetate (10:1) to afford **5** and **6** (6.165 g of the mixture) in 52.8% yield. GC showed a purity >98% and *Z*:*E* = 94:6.

IR spectrum (ν_{max}, cm^{-1}): 3347, 3007, 2926, 2855, 1462, 1057, 722.

PMR spectrum (δ, ppm, J/Hz): 5.31-5.45 (2H, m, CH=CH), 3.55 (2H, t, J = 6.4, $–CH_2–O$), 1.99-2.02 (2H, m, $CH_2–CH=CH$), 1.95-1.98 (2H, m, 10-CH_2), 1.44-1.52 (2H, m, 2-CH_2), 1.32-1.35 (2H, m, 9-CH_2), 1.27-1.32 [12H, m, $–(CH_2)_6$], 0.96 (3H, t, J = 8, CH_3).

Synthesis of (*Z/E*)-11-Tetradecen-1-ol Acetates 1 and 2. A mixture of **5** and **6** (6.000 g, 0.028 mol) was acetylated for 15 h by acetic anhydride (6 mL, 0.063 mol) in the presence of pyridine (15 mL) [11, 12] with stirring at room temperature, poured into icewater (50 mL), and extracted with ether. The organic layer was washed with water (20 mL) and saturated NaCl solution (20 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo. The products were purified by flash chromatography over a column of silica gel (100-200 mesh) with elution by petroleum ether-ethylacetate (30:1) to afford a mixture of **1** and **2** (6.60 g, 92.7%) as a colorless oil. GC showed a purity >98% with *Z*:*E* = 94:6.

IR spectrum (ν_{max}, cm^{-1}): 3005, 2961, 2926, 1743, 1464, 1365, 1238, 1037, 972 (s, *trans*-C=C), 731 (*cis*-C=C).

PMR spectrum (δ, ppm, J/Hz): 5.31-5.45 (2H, m, CH=CH), 4.05 (2H, t, J = 7.4, $CH_2–O$), 2.01-2.06 (3H, s, $O=C–CH_3$), 1.96-1.99 (4H, m, $–CH_2–C=C–CH_2–$), 1.59-1.64 (2H, m, 2-CH_2), 1.27-1.33 (16H, m, 8CH_2), 0.96 (3H, t, J = 8, CH_3).

^{13}C NMR spectrum (CD_3COCD_3, δ): 171.18 (O–C=O), 131.46, 129.25 (C11, C12), 66.42 (C1), 35.55 (C13), 33.36 (C10), 30.43, 30.33, 30.15, 29.91, 29.82, 28.63, 27.45, 26.58 (C2-C9), 17.28 ($O=CCH_3$), 14.35 (C14).

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