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SYNTHESIS OF 5*Z*,9*E*-TRIDECADIEN-1-YLACETATE, AN ATTRACTANT OF *Trichoplusia ni*

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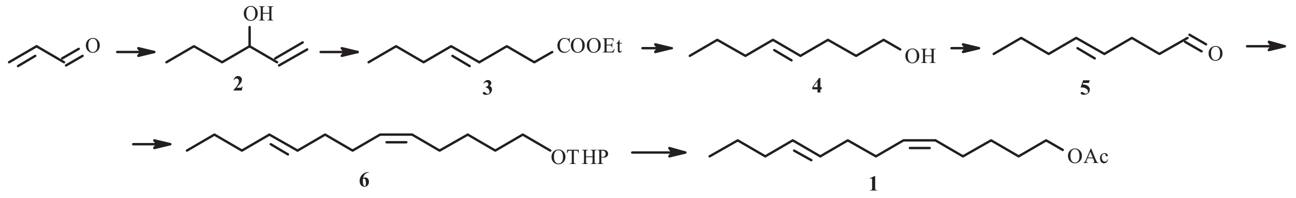
*A new synthetic scheme for 5*Z,9*E-tridecadien-1-ylacetate, an attractant of the cabbage looper* Trichoplusia ni *(Huebner) was developed using a highly stereoselective Claisen rearrangement.*

Keywords: insect pheromones, cabbage looper (*Trichoplusia ni*), 5*Z*,9*E*-tridecadien-1-ylacetate, Claisen rearrangement, Wittig reaction.

5*Z*,9*E*-Tridecadien-1-ylacetate (**1**) is an attractant of the male cabbage looper (*Trichoplusia ni* Huebner) that affects their mating behavior [1]. Only one synthetic method for this compound that uses the so-called acetylene method has been reported [1].

We developed a new synthetic scheme for **1** that uses as the key step the construction of a double bond with the *E*-configuration via the orthoester version of the Claisen rearrangement.



The starting material in the proposed scheme was 1-hexen-3-ol (**2**), which was readily obtained from reaction of propylmagnesium bromide and acrolein. The Claisen rearrangement occurred easily upon heating allylic alcohol **2** with triethylorthoacetate in the presence of a catalytic amount of propionic acid. This produced the ethyl ester of 4*E*-octenoic acid (**3**). The stereochemical purity of **3** was confirmed by GC and IR and PMR spectral data. In particular, the IR spectrum of **3** exhibited a single absorption band with $\nu = 965\ \text{cm}^{-1}$ in the region of double bond bending vibrations. This was characteristic of *trans* compounds. A band with $\nu = 780\ \text{cm}^{-1}$, characteristic of *cis* compounds, was not observed. Next, **3** was converted to the target molecule using a Wittig reaction through the two intermediates 4*E*-octen-1-ol (**4**) and 4*E*-octenal (**5**). The reaction of **5** with the ylide generated from 1-bromo-5-(tetrahydropyran-2-yl)oxypentane produced 5*Z*,9*E*-tridecadien-1-ol tetrahydropyranyl ether (**6**), which was converted in one step to the target compound **1** upon reaction with AcCl–AcOH. The overall yield of **1** was 15.5% calculated per starting acrolein.

EXPERIMENTAL

IR spectra were recorded in thin layers on a Beckman Microlab 620 MX instrument. PMR spectra were taken in $(CD_3)_2CO$ solution with HMDS internal standard on a Tesla BS-587A spectrometer (operating frequency 80 MHz). Chemical shifts are given on the δ scale. GC was performed on a Chrom-5 instrument with a flame-ionization detector, column (3500 × 3 mm), silicone liquid SE-30 (5%) stationary phase on chromaton N-AW-DMCS (0.16–0.20 mm), operating temperature 50–250°C, and He carrier gas (30 mL/min). TLC was performed on Silufol UV-254 plates with a fixed layer of SiO_2.

1-Hexen-3-ol (2). The Grignard reagent obtained from propylbromide (24.6 g, 0.2 mol), Mg (4.86 g, 0.2 mol), and anhydrous Et_2O (300 mL) was stirred vigorously, cooled (–10° to –15°C), treated dropwise with acrolein (11.2 g, 0.2 mol) in

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anhydrous Et_2O (40 mL) over 1 h, stirred for 1 h, refluxed for 0.5 h, cooled to 0°C, and decomposed with icewater (70 mL). The aqueous layer was separated and extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with a small quantity of saturated NaCl solution (30 mL), dried over Na_2SO_4, and evaporated. The residue was distilled to afford **2** (14.2 g, 71%), bp 135–136°C [2]. The IR and PMR spectra were analogous to those published [3].

4*E*-Octenoic Acid Ethyl Ester (3). A mixture of **2** (8.42 g, 84.2 mmol), triethylorthoacetate (50.6 g, 289 mmol), and propionic acid (0.2 g) was stirred at 135–137°C for 2 h, collecting the released EtOH through a fractionating column equipped with a condenser. The mixture was cooled to room temperature, treated with Et_2O (150 mL), washed successively with saturated $NaHCO_3$ and NaCl solutions, dried over $MgSO_4$, and evaporated. The residue was vacuum distilled to afford **3** (10.88 g, 76%), bp 104°C (10 mm Hg). IR spectrum (ν, cm^{-1}): 1745 (C=O), 1645, 965 (*E*-CH=CH). PMR spectrum (δ, ppm, J/Hz): 0.86 (3H, t, J = 6, CH_3), 1.13 (3H, t, J = 6, $\underline{CH_3}CH_2O$), 1.3–1.5 (2H, m, CH_2), 1.7–2.0 (4H, m, $H_2CC{=}CCH_2$), 2.24 (2H, t, J = 2, CH_2COO), 4.02 (2H, q, J = 6, CH_2O), 5.4–5.8 (2H, m, HC=CH) [4].

4*E*-Octen-1-ol (4). A suspension of $LiAlH_4$ (1.45 g, 39.6 mmol) in anhydrous Et_2O (100 mL) was stirred (under Ar), cooled (0–5°C), treated dropwise over 1 h with **3** (6.44 g, 37.9 mmol), heated to room temperature, stirred for another 2 h, cooled to 0°C, and treated dropwise over 0.5 h with H_2O (20 mL). The solution was decanted. The residue was washed with Et_2O (20 mL). The combined Et_2O layers were washed with saturated NaCl solution (3 × 50 mL), dried over Na_2SO_4, and evaporated. The residue was vacuum distilled to afford **4** (3.59 g, 74%), bp 108°C (13 mm) [5]. The IR and PMR spectra were analogous to those published [6].

4*E*-Octenal (5). A suspension of pyridinium chlorochromate (10.74 g, 4.96 mmol) in dry $CHCl_3$ (100 mL) was treated dropwise over 2 h with **4** (2.54 g, 19.8 mmol), diluted with Et_2O (100 mL), and passed over a column of silica gel (15 cm). The resulting solution was washed successively with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, and evaporated. The residue was chromatographed over a column of silica gel (eluent hexane:Et_2O, 8:2) to afford aldehyde **5** (2.02 g, 81%). The IR and PMR spectra were analogous to those published [6, 7].

1-(Tetrahydropyran-2-yl)oxy-5*Z*,9*E*-tridecadiene (6). 1-(Tetrahydropyran-2-yl)oxy-5-bromopentane (1.62 g, 6.45 mmol) (prepared as before [8]) and PPh_3 (1.69 g, 6.45 mmol) were heated at 160°C for 8 h in an ampul under Ar. The contents were cooled, transferred to a flask, treated with anhydrous THF (50 mL), treated carefully under Ar at –30°C with *t*-BuOK (0.72 g, 6.45 mmol), stirred for 0.5 h, cooled to –70°C, treated with **5** (0.83 g, 6.45 mmol), stirred for 3 h, heated to room temperature, left overnight, diluted with hexane (50 mL), filtered through a fritted-glass filter, and evaporated. The residue was chromatographed over a column of silica gel (eluent hexane then hexane:Et_2O, 8:2) to afford **6** (1.08 g, 60%). IR spectrum (ν, cm^{-1}): 1640, 970 (*E*-CH=CH), 780 (*Z*-CH=CH). PMR spectrum (δ, ppm, J/Hz): 0.88 (3H, t, J = 6, CH_3), 1.2–1.6 (12H, m, $6 \times CH_2$), 1.8–2.1 (8H, m, $CH_2C{=}C$), 3.6–3.9 (4H, m, CH_2O), 4.83 (1H, m, CH), 5.1–5.6 (4H, m, HC=CH).

5*Z*,9*E*-Tridecadien-1-ylacetate (1). A mixture of **6** (0.62 g, 2.21 mmol), AcOH (1.5 mL), and AcCl (0.35 mL) was refluxed for 5 h (TLC monitoring), cooled, treated with icewater, and extracted with Et_2O (3 × 20 mL). The extract was washed successively with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, and evaporated. The residue was chromatographed over a column of silica gel (eluent hexane:Et_2O, 8:2) to afford **1** (0.42 g, 80%). IR spectrum (ν, cm^{-1}): 1750 (C=O), 1640, 970 (*E*-CH=CH), 780 (*Z*-CH=CH). PMR spectrum (δ, ppm, J/Hz): 0.88 (3H, t, J = 6, CH_3), 1.2–1.6 (6H, m, $3 \times CH_2$), 1.8–2.1 (11H, m, CH_3COO, $4 \times CH_2C{=}C$), 3.6–3.9 (2H, m, CH_2O), 5.1–5.6 (4H, m, 2 × HC=CH) [1].

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