

**SYNTHESIS OF 4E,7Z-TRIDECADIEN-1-YLACETATE,
A COMPONENT OF THE *Phthorimaea operculella*
SEX PHEROMONE**

R. R. Vakhidov and I. N. Musina

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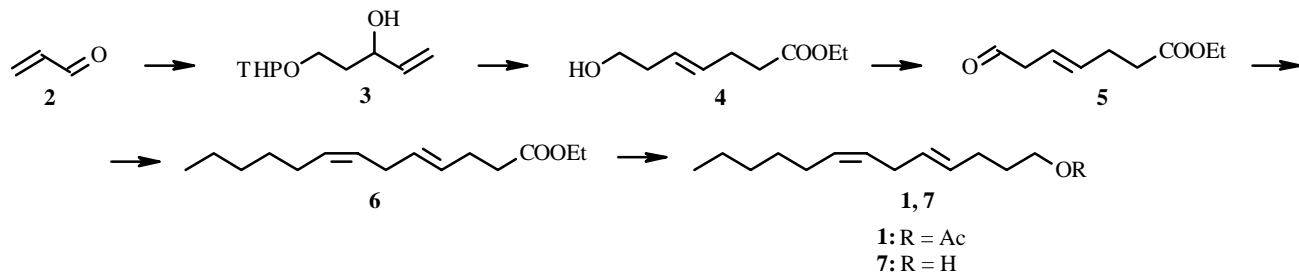
A new synthetic approach to 4E,7Z-tridecadien-1-ylacetate, a component of the Phthorimaea operculella (Zeller) potato moth sex pheromone, was developed using a highly stereoselective Claisen rearrangement and Wittig reaction.

Key words: *Phthorimaea operculella*, 4E,7Z-tridecadien-1-ylacetate, synthesis.

4E,7Z-Tridecadien-1-ylacetate (**1**) has been identified as a component of the sex pheromone of the potato moth *Phthorimaea operculella* (Zeller), a potato pest [1]. Several syntheses of this compound have been reported [2-14].

The new synthesis of **1** that was developed by us is based on a thermal Claisen rearrangement of secondary allyl alcohols and is highly recommended as a stereospecific method for constructing a double bond with the (*E*)-configuration [4].

The starting material was acrolein (**2**), which reacted with the Grignard reagent generated from the tetrahydropyran ether of 2-bromoethan-1-ol to give the key synthon, alkenic secondary alcohol **3**. Thermal Claisen rearrangement occurred smoothly upon heating of **3** with triethylorthoacetate in the presence of catalytic amounts of propionic acid for 1 h at 138°C. Removal of the THP protecting group produced unsaturated alcohol **4** with exclusively the *E*-configuration, as confirmed by GC and IR and PMR spectra. In particular, the absorption band of C=C vibrations appeared at 965 cm⁻¹ whereas it was 780 cm⁻¹ for the analogous compound with the *Z*-configuration. Then, **4** was oxidized to aldehyde **5** using pyridinium chromate. A Wittig reaction of **5** with the phosphorus ylide generated from hexylbromide gave diene ester **6** with the 7Z-configuration for the double bond. The final step was hydride reduction of the ester in **6** and acetylation of the resulting 4E,7Z-tridecadien-1-ol (**7**) to give **1**.



According to capillary GC, **1** contains at least 99% of the main product, the structure of which was confirmed by IR and PMR spectroscopy.

EXPERIMENTAL

IR spectra of thin layers were recorded on a Microlab 620 MX (Beckman) instrument. PMR spectra were obtained in (CD₃)₂CO on a Tesla BS-587A spectrometer (working frequency 80 MHz). Chemical shifts are given on the δ scale with

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HMDS internal standard. GC was carried out on a Chrom-5 instrument with a flame-ionization detector, 3500 × 3 mm column, SE-30 (5%) stationary phase on Chromaton N-AW-DMCS (0.16-0.20 mm), working temperature 50-250°C, He carrier gas (30 mL/min). Compounds **1**, **4**, and **7** were analyzed on a Carlo Erba instrument with a glass capillary column (20 m × 0.2 mm) and working temperature 50-200°C. TLC was performed on Silufol plates with a fixed layer of SiO₂.

1-(Tetrahydropyran-2-yl)hydroxypent-4-en-3-ol (3). The Grignard reagent prepared from the THP ether of 2-bromoethan-1-ol (6.27 g, 30.0 mmol), Mg (0.80 g, 33 mmol), and dry diethylether (100 mL) was cooled; treated dropwise with acrolein (1.68 g, 30 mmol) in absolute diethylether (20 mL); stirred for 1 h; and treated with cold water (20 mL). The aqueous layer was separated and extracted with diethylether (3 × 20 mL). The combined organic layer was dried over Na₂SO₄. The solvent was evaporated. The residue was chromatographed over silica gel to afford **3** (4.53 g, 81%).

IR spectrum (ν , cm⁻¹): 3500 (OH), 1640 and 970 (CH=CH₂).

PMR spectrum (δ , ppm): 1.2-1.5 (8H, m, CH₂), 3.6-4.2 (5H, m, CH₂-O, CH-O), 4.84 (1H, m, O-CH-O), 5.1-5.4 (2H, m, CH₂=C), 5.6-5.9 (1H, m, CH=C).

Ethyl-7-hydroxyhept-4E-enoate (4). A mixture of **3** (3.73 g, 20.0 mmol), triethylorthoacetate (9.68 g, 6.0 mmol), and propionic acid (0.02 g) was heated on an oil bath at 138°C for 1 h. The ethanol that was formed was removed through a fractionating condenser. The mixture was cooled, treated with diethylether (100 mL), washed with saturated NaHCO₃ and NaCl solutions, dried over Na₂SO₄, and evaporated. Unreacted triethylorthoacetate was distilled off in vacuo. The residue was diluted with diethylether (100 mL), treated with TsOH (0.2 g), stirred at room temperature for 24 h (TLC monitoring), treated with saturated NaHCO₃ and NaCl solutions, dried over Na₂SO₄, and evaporated. The residue was chromatographed over silica gel to afford **4** (19.3 g, 56%).

IR spectrum (ν , cm⁻¹): 3500 (OH), 1740 (C=O), 1650 and 965 (E-CH=CH).

PMR spectrum (δ , ppm, J/Hz): 1.12 (3H, t, J = 6, CH₃), 1.8-2.1 (6H, m, CH₂C=CH₂, CH₂COO), 3.6-4.1 (5H, m, CH₂-O, O-H), 5.2-5.5 (2H, m, CH=CH).

Ethyl-7-oxo-4E-heptenoate (5). A suspension of pyridinium chromate (16.45 g, 9.21 mmol) in dry CHCl₃ (100 mL) was treated dropwise with **4** (1.70 g, 7.86 mmol) over 5 min, stirred for another 30 min, diluted with diethylether (100 mL), passed over a column of silica gel (15 cm layer), washed successively with NaHCO₃ and NaCl solutions, dried over Na₂SO₄, and evaporated. The residue was chromatographed over silica gel to afford **5** (0.83 g, 62%).

IR spectrum (ν , cm⁻¹): 1740 (C=O), 1650 and 965 (E-CH=CH).

PMR spectrum (δ , ppm, J/Hz): 1.12 (3H, t, J = 6, CH₃), 1.8-2.2 (4H, m, CH₂C=C, CH₂COO), 3.6-4.3 (4H, m, CH₂O, C=C-CH₂-C=O), 5.2-5.5 (2H, m, CH=CH), 9.3 (1H, s, CH=O).

Ethyl-4E,7Z-tridecadienoate (6). Hexylbromide (0.69 g, 4.18 mmol) and PPh₃ (1.10 g, 4.18 mmol) in a flask under Ar were heated at 160°C for 8 h, cooled to -20°C, and treated with absolute THF (50 mL). *t*-BuOK (0.46 g, 4.18 mmol) was carefully added at -20°C. The mixture was stirred for 30 min, cooled to -70°C, treated with **5** (0.71 g, 4.18 mmol), stirred at -70°C for 2 h, left overnight, diluted with hexane (50 mL), filtered through a Schott filter to remove Ph₃PO, evaporated, and chromatographed over a column of silica gel to afford **6** (0.63 g, 64%). IR and PMR spectra were analogous to those published [12].

4E,7Z-Tridecadien-1-ol (7) and **4E,10Z-tridecadien-1-ylacetate (1)** were synthesized and characterized as before [12].

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