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Stereoselective Synthesis of 11(*E*)-Tetradecen-1-yl Acetate—Sex Pheromone of Sod Webworm (*Loxostege sticticalis*)

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Abstract—On the basic of Claisen rearrangement using orthoesters we carried out stereoselective synthesis of 11(*E*)-tetradecen-1-yl acetate, a sex pheromone of sod webworm (*Loxostege sticticalis*), which is a specially dangerous pests of crops.

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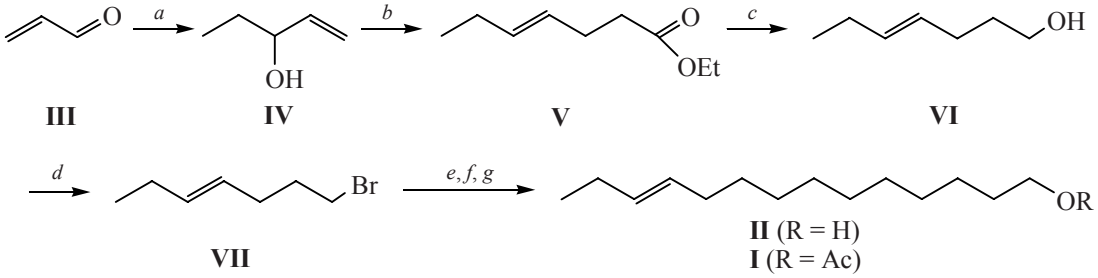
11(*E*)-Tetradecen-1-yl acetate **I** is identified as a sex pheromone of sod webworm (*Loxostege sticticalis*) [1], a basic component of pheromones of omnivorous leaf roller moths (*Archips podana*) [2], plant moths (*Ostrinia nubilalis*) [3], fir leaf roller moths (*Choristoneura fumiferana*) [4] and some others dangerous pests species. In literature some syntheses of acetate **I** and its precursor 11(*E*)-tetradecen-1-ol **II** using acetylene way [5–7], Wittig reaction and its modifications [8, 9], various cross-coupling reactions on the matrix of Grignard reagents [10–13], organoboron compounds [14, 15] and isomerization of 11(*Z*)-tetradecen-1-yl acetate into the required *trans*-isomer [16] have been described. For the most of them a low selectivity is characteristic on the stage of double bond formation.

In this work synthesis of pheromone was carried out on the basis of Claisen orthoester rearrangement, which has a reputation as stereospecific way to obtain carboxylates having trans-bond in 4-position. On the matrix of these products, by their transformation into the corresponding 4(*E*)-alkenyl bromides followed by coupling with respective α,ω-bifunctional compound one can produce compounds containing double bond, which is the more remote from the functional group than in the initial product of Claisen rearrangement.



EtMgBr (*a*); $CH_3C(OEt)_3$, CH_3COOH (*b*); $LiAlH_4$ (*c*); $PhP_3{\cdot}Br_2$ (*d*); $(CH_2)_7MgBr$, CuI/2,2'-bipy (*e*); MeOH/TsOH (*f*); Ac_2O/Py (*g*).

In this scheme of synthesis the available acrolein **III** was used as initial compound. Its combination with Grignard reagent ethylmagnesium bromide gives rise to 1-penten-3-ol **IV** with good yield. Rearrangement of the secondary allyl alcohol **IV** proceeds smoothly upon the heating with triethyl orthoacetate in the presence of acetic acid to form ethyl 4(*E*)-heptenoate **V**. Stereochemical purity of the latter was proved with GLC analysis on a capillary column. *trans*-Configuration of the formed double bond is unambiguously confirmed by the presence of a strong absorption band at 968 cm^{-1} in the IR spectrum of ester **V** belonging to out-of-plane

bending vibrations of H–C= bond (*E*-configuration), and by the absence of characteristic absorption of double bond (*Z*-configuration) at 660–730 cm^{-1}.

The following transformations of synton **V** included hydride reduction and conversion of 4(*E*)-hepten-1-ol **VI** into the corresponding bromide **VII**. Reaction of the latter with the Grignard reagent generated from 1-bromo-7-[(tetrahydro-2*H*-pyran-2-yl)-oxy]heptane (synthesized according to [17]) followed by acidic hydrolysis of the coupling product obtained resulted in 11(*E*)-tetradecen-1-ol **II**, which was transformed into the target acetate **I** by standard way. Overall yield of pheromone is 33.5% calculating on the initial acrolein.

Aiming at the exhaustive confirming of pheromone **I** (*E*)-configuration, its (*Z*)-analogue was additionally synthesized (accordingly to procedure [18]). In the ^{13}C NMR spectrum of 11(*Z*)-tetradecen-1-yl acetate the signals at δ 20.48 and 27.06 ppm correspond to allyl C-atoms (C^{13} and C^{10} respectively), while in the pheromone **I** spectrum they are at δ 25.52 (C^{13}) and 32.49 (C^{10}) ppm respectively. This characteristic shift of *trans*-alkenes allyl C-atoms signals by 5 ppm downfield was already noticed in literature [19]. This fact may be used as an exhaustive proof of the unsaturated compounds steric configuration.

EXPERIMENTAL

The IR spectra were taken on a IRPrestige-21 SHIMADZU Fourier-spectrophotometer from thin film. The ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Bruker AM-300 device (operating frequency 300 and 75.47 MHz respectively) relative to internal TMS. Chromatographic and mass-spectral analysis was carried out on a Khromatek-Kristall 5000 apparatus-program complex using Finnigan DSQ mass-selective detector (70 eV) and Restek Rtx-5ms capillary column (5% phenyl-, 95% dimethylpolysiloxane, length 15 m). Evaporator temperature is 250°C, ionization camera temperature 250°C. Analysis was carried out in temperature programming mode from 50 to 250°C with the rate 10°C/min; carrier gas is helium (1.1 ml min^{-1}).

1-Penten-3-ol (IV). To a Grignard reagent obtained from 10.9 g (0.1 mol) of ethyl bromide and 2.43 g (0.1 mol) of magnesium raspings in 100 ml of absolute diethyl ether was slowly added 5.61 g (0.1 mol) of acrolein **III** in 20 ml of absolute diethyl ether under vigorous stirring and cooling to –15°C for 1 h. This mixture was stirred at room temperature for 1 h, cooled to 0°C and then 50 ml of water was carefully added. Organic layer was separated and water layer was extracted with ether (3×50 ml). Organic layers obtained were dried over $MgSO_4$ and evaporated. Then residue was distilled. Yield 7.01 g (81%), bp 114–116°C, n_D^{20} 1.4241. IR spectrum, ν, cm^{-1}: 3354 (OH), 3080, 2965, 2934, 2878, 1844, 1647 (C=C), 1458, 1425, 1067, 991, 972, 922, 860. ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* 7.4 Hz), 1.48–1.58 m (2H, CH_2CHOH), 2.19 s (1H, OH), 3.99 q (1H, $CHOH$, *J* 6.3 Hz), 5.08 d (1H, *trans*-HC^1=, *J* 10.3 Hz), 5.18 d (1H, *cis*-HC^1=, *J* 17.2 Hz), 5.77–5.88 m (1H, HC^2=). ^{13}C NMR spectrum, δ, ppm: 9.47 (C^5), 29.74 (C^4), 74.41 (C^3), 114.59 (C^1), 140.96 (C^2). Mass-spectrum, *m/z* (I_{rel}, %): 58 (5.62), 57 (100), 43 (7.48), 41 (8.82), 39 (7.35), 31 (12.82), 29 (31.44), 27 (14.29).

Ethyl 4(*E*)-heptanoate (V). A mixture of 4.31 g (0.05 mol) of alcohol **IV**, 24.33 g (0.15 mol) of triethyl orthoacetate and 0.1 g of acetic acid was stirred for 6 h at 110°C, distilling off ethanol released. The reaction mixture was cooled to room temperature and 50 ml of diethyl ether was added. Then mixture was sequentially washed with $NaHCO_3$ and NaCl saturated solutions, dried over $MgSO_4$ and concentrated. The residue obtained was distilled under vacuum. Yield 6.46 g (83%), bp 130–132°C (100 mm Hg). IR spectrum, ν, cm^{-1}: 2965, 2934, 2874, 2853, 1738 (C=O), 1447, 1373, 1250, 1165, 1040, 968 (*trans*-HC=). ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.5 Hz), 1.22 t (3H, CH_3CH_2O, *J* 7.2 Hz), 1.96 t (2H, CH_2C=O, *J* 7.4 Hz), 2.23-2.36 m (4H, CH_2CH=), 4.10 q (2H, CH_2O, *J* 7.1 Hz), 5.32–5.53 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: 13.68 (C^7), 14.15 (CH_3CH_2O), 25.44 (C^6), 27.84 (C^3), 34.55 (C^2), 60.10 (CH_3CH_2O), 126.91 (C^4), 133.21 (C^5), 173.15 (C^1). Mass-spectrum, *m/z* (I_{rel}, %): 156 (16.07), 111 (21.00), 110 (45.23), 88 (61.48), 85 (26.53), 83 (47.61), 82 (59.18), 81 (55.71), 70 (37.02), 69 (73.26), 68 (93.95), 67 (92.41), 61 (34.52), 60 (55.95), 57 (13.14), 55 (100), 54 (17.76).

4(*E*)-Hepten-1-ol (VI). To a solution of 0.417 g (11 mmol) of $LiAlH_4$ in 50 ml of absolute diethyl ether was added 3.124 g (20 mmol) of ester **V** under stirring and cooling (Ar, 0°C) for 1 h. The reaction mixture was heated to room temperature, stirred for 2 h, cooled to 0°C and then 20 ml of water was carefully added for 0.5 h. Organic layer was separated, washed with NaCl saturated solution, dried over $MgSO_4$ and concentrated. Yield 1.967 g (86%), n_D^{20} 1.4426. IR spectrum,

ν, cm^{-1}: 3342 (OH), 2893, 2872, 2848, 1717, 1589, 1440, 1375, 1215, 1059, 966 (*trans*-HC=). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH_3, *J* 7.4 Hz), 1.53–1.62 m (2H, CH_2CH_2O), 1.91–2.05 m (4H, CH_2CH=), 2.74 s (1H, OH), 3.57 t (2H, CH_2OH, *J* 6.6 Hz), 5.31–5.50 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: 13.80 (C^7), 25.42 (C^6), 28.71 (C^3), 32.35 (C^2), 62.11 (C^1), 128.35 (C^4), 132.49 (C^5). Mass-spectrum, *m/z* (I_{rel}, %): 114 (3.15), 96 (19.44), 81 (100), 79 (15.79), 68 (23.72), 67 (32.08), 57 (10.79), 55 (35.81), 54 (21.29), 53 (12.91).

1-Bromo-4(*E*)-heptene (VII). To a solution of 2.211 g (8.43 mmol) of triphenylphosphine in 40 ml of chloroform was added solution of 1.347 g (8.43 mmol) of bromine in 10 ml of chloroform under stirring and cooling (Ar, 10°C). To the formed suspension of $PPh_3 \cdot Br_2$ was added 0.936 g (8.2 mmol) of alcohol **VI** in 10 ml of chloroform and this mixture was stirred for 3 h at room temperature under argon. Then mixture was diluted with 150 ml of hexane, filtered and filtrate was concentrated. The residue was purified by column chromatography (SiO_2, pentane). Yield 1.338 g (92%), n_D^{20} 1.4733. IR spectrum, ν, cm^{-1}: 2963, 2932, 2872, 2847, 1437, 1238, 1055, 968 (*trans*-HC=), 648, 565 (CBr). ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.4 Hz), 1.87–2.06 m (4H, CH_2CH=), 2.11–2.19 m (2H, CH_2CH_2Br), 3.41 t (2H, CH_2Br), 5.30-5.58 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: 13.80 (C^7), 25.53 (C^6), 30.79 (C^3), 32.46 (C^2), 33.19 (C^1), 126.85 (C^4), 133.67 (C^5). Mass-spectrum, *m/z* (I_{rel}, %): 178 (12.17), 176 (12.86), 97 (45.03), 81 (33.76), 69 (45.37), 67 (22.55), 55 (100), 54 (16.63), 53 (13.93).

11(*E*)-Tetradecen-1-ol (II). To a suspension of 0.160 g (0.84 mmol) of CuI in 6 ml of absolute THF was added 0.131 g (0.84 mmol) of 2,2'-bipyridyl. The mixture was stirred for 0.5 h under argon atmosphere at 20°C, cooled to 2°C and a solution of 0.745 g (4.21 mmol) of bromide **VII** in 3 ml of absolute THF was added. The reaction mixture was stirred for 15 min followed by dropwise addition for 1 h of Grignard reagent prepared from 1.527 g (5.47 mmol) of 1-bromo-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]heptane (prepared accordingly to [17]) and 0.146 g (6 mmol) of magnesium raspings in 5 ml of absolute THF. The reaction mixture was stirred for 2 h at 2°C and 6 h at room temperature. Then 10 ml of NH_4Cl saturated solution was added and mixture was stirred for 1 h. Organic layer was separated and water layer was extracted with ether (3×10 ml). Organic solution was concentrated; residue was dissolved in 20 ml of methanol containing 0.05 g of TsOH. This mixture was stirred at room temperature for 24 h and concentrated. To the residue was added 50 ml of diethyl ether followed by washing with $NaHCO_3$ and NaCl saturated solutions, drying over Mg_2SO_4 and concentrating. The residue obtained was chromatographically purified (SiO_2, hexane–ether, 1:1). Yield 0.602 g (67%), n_D^{20} 1.4562. IR spectrum, ν, cm^{-1}: 3335 (OH), 2961, 2926, 2853, 1458, 1057, 964 (*trans*-HC=). ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.3 Hz), 1.21–1.41 m (14H, CH_2), 1.50-1.61 m (2H, CH_2CH_2OH), 1.91–2.06 m (4H, CH_2CH=), 3.39 s (1H, OH), 3.64 t (2H, CH_2OH, *J* 6.6 Hz), 5.34–5.48 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: 13.91 (C^{14}), 25.52 (C^{13}), 25.70 (C^3), 29.11 (CH_2), 29.39 (CH_2), 29.45 (CH_2), 29.50 (CH_2), 29.55 (CH_2), 29.59 (CH_2), 32.50 (C^{10}), 32.71 (C^2), 62.83 (C^1), 129.31 (C^{11}), 131.80 (C^{12}). Mass-spectrum, *m/z* (I_{rel}, %): 96 (25.74), 95 (26.66), 82 (48.17), 81 (35.47), 69 (31.24), 68 (44.86), 67 (54.38), 55 (100), 54 (31.60), 43 (33.06), 41 (96.59).

11(*E*)-Tetradecen-1-yl acetate (I). A mixture of 0.367 g (1.73 mmol) of alcohol **II**, 1.23 g of absolute pyridine and 0.88 g of acetic anhydride was stirred at room temperature for 24 h. Then 20 ml of diethyl ether was added and mixture was sequentially washed with $NaHCO_3$ and NaCl saturated solutions, dried over Mg_2SO_4 and concentrated. The residue was chromatographically purified (SiO_2, hexane–ether, 9:1). Yield 0.414 g (94%), n_D^{20} 1.4481. IR spectrum, ν, cm^{-1}: 2957, 2926, 2853, 1744 (C=O), 1366, 1238, 1040, 966 (*trans*-HC=). ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, *J* 7.4 Hz), 1.22–1.43 m (14H, CH_2), 1.58–1.71 m (2H, CH_2CH_2O), 1.94–2.18 m (7H, CH_3C=O, CH_2CH=), 4.06 t (2H, CH_2O, *J* 6.6 Hz), 5.34–5.50 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: 13.91 (C^{14}), 20.86 (CH_3C=O), 25.52 (C^{13}), 25.85 (C^3), 28.57 (C^2), 29.09 (CH_2), 29.18 (CH_2), 29.43 ($3CH_2$), 29.59 (CH_2), 32.49 (C^{10}), 64.55 (C^1), 129.28 (C^{11}), 131.82 (C^{12}), 171.04 (C=O). Mass-spectrum, *m/z* (I_{rel}, %): 96 (34.41), 82 (72.55), 81 (37.93), 69 (29.43), 68 (77.45), 67 (52.06), 55 (62.13), 43 (100), 41 (58.77).

11(*Z*)-Tetradecen-1-yl acetate was prepared by [18]. ^{13}C NMR spectrum, δ, ppm: 14.35 (C^{14}), 20.48 (C^{13}), 20.97 (CH_3C=O), 25.88 (C^3), 27.06 (C^{10}), 28.59 (C^2), 29.22 ($2CH_2$), 29.48 ($3CH_2$), 29.74 (CH_2), 64.63 (C^1), 129.28 (C^{11}), 131.50 (C^{12}), 171.19 (C=O).

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