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INSECT PHEROMONES AND THEIR ANALOGS.
LVIII. SYNTHESIS OF HEXADECA-7Z,11E-DIEN-1-YL ACETATE — A COMPONENT OF THE SEX PHEROMONES OF *Pectinophora gossypiella* AND *Sitotroga cerealella*

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*A new synthesis of hexadeca-7Z,11E-dien-1-yl acetate — a component of the sex pheromones of the pink bollworm (*Pectinophora gossypiella*) and the Angoumois grain moth (*Sitotroga cerealella*) — is proposed that is based on a thermal Claisen rearrangement.*

Hexadeca-7Z,11E-dien-1-yl acetate (**1**) is a component of the sex pheromones of the pink bollworm (*Pectinophora gossypiella*) and the Angoumois grain moth (*Sitotroga cerealella*) [1-4].

A number of syntheses of compound (**1**) using for the construction of double bond with the required configuration the acetylene route [5-8], the Wittig reaction or modifications of it [9-15], or the ozonolysis of cyclic butadiene oligomers have been described in the literature [16].

The new synthesis of pheromone (**1**) that we have developed is based on the thermal Claisen rearrangement of secondary allyl alcohols, which has recommended itself as a highly selective method for constructing a double bond with the (E)-configuration in position 4 with respect to a functional group and which we have used in the synthesis of tridec-4E-en-1-yl acetate [17]. This approach, in combination with the Wittig olefination of an (E)-Δ^4-aldehyde, opens up a simple route to dimethyl-separated alkadiene compounds with the (Z, E)-configuration. As the initial compound in the proposed scheme of synthesis we used hept-1-en-3-ol (**2**), which is readily obtained from *n*-butyl bromide and acrolein [18]. Heating the alcohol (**2**) with triethyl orthoacetate in the presence of catalytic amounts of propionic acid led to the occurrence of a smooth Claisen rearrangement giving ethyl non-4E-enoate (**3**).

The stereochemical purity of ester (**3**) was confirmed by GLC analysis on a capillary column and by its IR and ^{1}H and ^{13}C NMR spectra. In the region of the deformation vibrations of double bonds of the IR spectrum of compound (**3**) there was a single absorption band (ν 965 cm^{-1}), which is characteristic for transoid compounds. The SSCC of the olefinic protons, 14 Hz, and also the presence in the ^{13}C NMR spectrum of a signal at δ 32.17 ppm that is characteristic for alkenes with the (E)-configuration, corresponding to the C_6 atom in the allyl position [19], unambiguously witnessed the fact that compound (**3**) belonged to the (E)-alkene series.

Then the ester (**3**) was converted in two stages through the intermediate alcohol non-4E-en-1-ol (**4**) into the non-4E-enal (**5**) that was required for the subsequent construction of the target molecule by means of the Wittig reaction. Its interaction with the ylide generated from 7-(tetrahydropyran-2-yloxy)heptyltriphenylphosphonium bromide under the action of potassium *tert*-butanolate led to the tetrahydropyranyl ether of hexadeca-7Z,11E-dien-1-ol (**6**), converted in one stage by interaction with a mixture of AcCl and AcOH into the desired pheromone (**1**):

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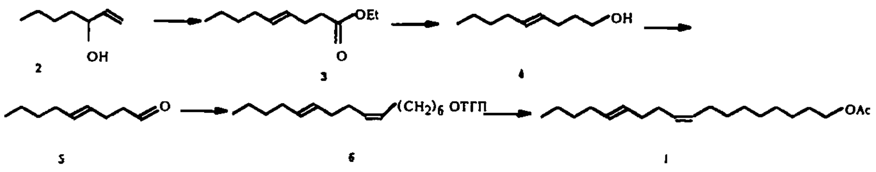

EXPERIMENTAL

IR spectra were taken on a Microlab 620 MX spectrometer (in a film), PMR spectra were recorded on a Tesla BS-587A instrument (working frequency 80 MHz, solvent $CDCl_3$ or $(CD_3)_2CO$ (for compound (4)): chemical shifts are given on the δ scale, with HMDS as internal standard. The ^{13}C NMR spectrum of compound (3) was recorded on a Bruker AM300 instrument, working frequency 75 MHz, solvent $CDCl_3$, internal standard TMS. GLC analyses were conducted on a Chrom-5 instrument with the stationary phase silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at a working temperature of 50-250°C, gas-carrier — gel. Also, analysis of compound (3) was conducted on a Chromotopac C-R3A instrument, stationary phase silicone liquid SE-30 at a working temperature of 50-250°.

Ethyl Non-4E-enoate (3). A mixture of 6.14 g (0.0539 mole) of the alcohol (2) (obtained according to [18]), 32.4 g (0.185 mole) of triethyl orthoacetate, and 0.2 g of propionic acid was stirred at 135-137°C for 2 h, the ethanol formed being led off through a stillhead fitted with a vertical condenser. The mixture was cooled to room temperature and, after the addition of 100 ml of diethyl ether, it was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, and evaporated. The residue was distilled in vacuum. This gave 7.64 g (77%) of the ester (3), bp 122-124°C (14 mm), cp. [18]. IR spectrum (ν, cm^{-1}): 1745 (C=O), 1645, 965 (E−CH=CH). PMR spectrum: 0.85 (t, 3H, J=6 Hz, CH_3), 1.12 (t, 3H, J=6 Hz, $\underline{CH_3}CH_2O$), 1.3-1.5 (m, 2H, 2 × CH_2), 1.75-2.05 (m, 4H, $H_2CC=CCH_2$), 2.22 (t, 2H, J=2 Hz, CH_2COO), 4.00 (q, 2H, J=6 Hz, H_2C-O), 5.4-5.8 (m, 2H, HC=CH). ^{13}C NMR 173.15 (C1), 131.72 (C5), 129.95 (C4), 60.13 (H_2C-O), 34.44 (C2), 32.17 (C6), 31.67 (C7), 27.94 (C3), 22.15 (C8), 14.22 ($\underline{CH_3}CH_2O$), 13.90 (C9).

Non-4E-en-1-ol. With stirring and cooling (0-5°C), 5.62 g (0.035 mole) of the ester (3) was added dropwise over 1 h to a suspension of 1.39 g (0.0366 mole) of $LiAlH_4$ in 100 ml of abs. diethyl ether, and the mixture was heated to room temperature and stirred for another 2 h. Then it was cooled to 0°C and 20 ml of water was added dropwise over 0.5 h. The solution was decanted off and the residue was washed with ether (20 ml), after which the combined ethereal solution was washed with saturated NaCl solution (3 × 50 ml), dried with Na_2SO_4, and evaporated. The residue was distilled in vacuum. This gave 3.38 g (78%) of the alcohol (4), bp 118°C (15 mm). Its IR and PMR spectra were similar to those given in [14].

Non-4E-enal (5). Over 2 h, 2.0 g (0.014 mole) of the alcohol (4) was added dropwise to a suspension of 7.58 g (0.035 mole) of pyridinium chlorochromate in 100 ml of dry chloroform, after which the reaction mixture was diluted with 100 ml of diethyl ether and passed through a layer of silica gel (15 cm). The resulting solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried over Na_2SO_4, and evaporated. The residue was distilled under vacuum. This gave 1.61 g (82%) of the aldehyde (5), bp 87-88°C (20 mm). IR spectrum (ν, cm^{-1}): 1765 (C=O), 1645, 970 (E−CH=CH). Its PMR spectrum was similar to that given in [20].

1-(Tetrahydropyran-2-yloxy)hexadeca-7,11-diene (6). A mixture of 1.63 g (0.00586 mole) of 7-(tetrahydropyran-2-yloxy)hept-1-yl bromide (obtained according to [21]) and 1.54 g (0.00586 mole) of PPh_3 was heated in a sealed tube under Ar at 160°C for 8 h. Then it was cooled and transferred to a flask, 50 ml of THF was introduced, and then, under argon at −30°C, 0.645 g (0.00586 mole) of *t*-BuOK was carefully added and the mixture was stirred for 0.5 h. After this, it was cooled to −70°C, and 0.82 g (0.00586 mole) of the aldehyde (5) was added and the resulting mixture was stirred for 3 h and was then heated to room temperature and left overnight. It was diluted with 50 ml of hexane, filtered through a Schott filter and evaporated, and the residue was chromatographed on a column of silica gel (eluents: hexane and then hexane−ether (8:2)). This gave 1.21 g (62%) of the ether (6). Its IR and NMR spectra were identical with those given in [20].

1-Acetoxyhexadeca-7Z,11E-diene (1). A mixture of 0.55 g of compound (6), 1.5 ml of AcOH, and 0.35 ml of AcCl was boiled for 5 h, and then ice-cooled water was added, the product was extracted with diethyl ether (3 × 20 ml), and the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried over Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2; eluent hexane−ether (8:2)). This gave 0.40 g (81%) of the ester (1) in the form of a colorless liquid. Its IR and PMR spectra were similar to those given in [21].

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