

temperature for 30 h. After the usual working up, the acetate was obtained; its yield after chromatography on silica gel [hexane-diether ether (3:1)] was 0.98 g (77.2), n_D^{20} 1.4432 (see [1]). IR spectrum (ν , cm^{-1}): 970 (trans-CH=CH), 1250, 1740 ($-\text{OCOCH}_3$). PMR spectrum (δ , ppm): 0.85 (3H, m, CH_3), 1.0-1.7 (16H, m, CH_2), 1.92 (3H, s, CH_3CO), 1.95 (4H, m, $\text{CH}_2-\text{C}=\text{C}$), 3.92 (2H, t, CH_2O , $J = 6.7$ Hz), 5.28 (2H, m, $\text{CH}=\text{CH}$).

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INSECT PHEROMONES AND THEIR ANALOGUES

XXVI. SYNTHESIS OF HEXADEC-11Z-EN-1-OL AND ITS ACETATE AND HEXADEC-11Z-EN-AL - COMPONENTS OF THE PHEROMONES OF INSECTS OF THE ORDER LEPIDOPTERA

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Pheromone components of insects of the genera Heliothis and Mamestra have been synthesized with the use of functionally differentiated ozonolysis of cyclododecene.

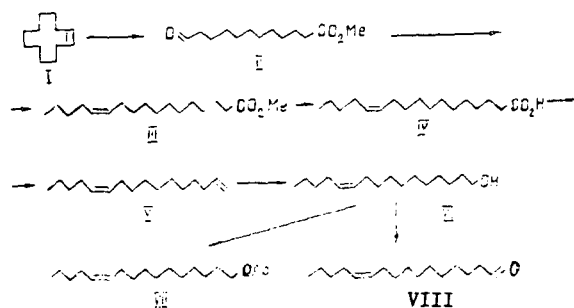
An approach to the synthesis of pheromones of the alk-Z-ene series based on the transformations of the products of the functionally differentiated ozonolysis of cyclic olefins [1] had been used in the synthesis of hexadec-11Z-en-1-ol (VI) and its acetate (VII) and of hexadec-11Z-enal (VIII) - components of the sex pheromones of ecologically harmful moths of the genera Mamestra and Heliothis.

The ozonolysis of cyclododecene (I) gave a high yield of methyl 11-oxododecanoate (II) [2], which was introduced into the Wittig reaction with n-amyldenetriphenylphosphorane, leading to methyl heptadec-12-enoate (III) exclusively with the Z- configuration, as was shown by the results of GLC analysis and the ^{13}C NMR spectrum.* This result on the stereochemistry of olefination confirmed results obtained previously for this reaction with esters of ω -formylcarboxylic acids [1].

Saponification of the ester function in (III) and subsequent oxidative decarboxylation by the action of lead tetraacetate and copper diacetate led to hexadeca-1,11Z-diene (V). Hydroboration of the diene (V) with the aid of 9-borabicyclo[3.3.1]nonane took place selectively at the terminal double bond and, after oxidation of the organoboron intermediate with a H_2O_2 -NaOH mixture, gave the desired alcohol (VI), by the acetylation of which the

*The stereochemical individuality of compound (III) was shown by the single peak in its GC chromatograms obtained on various columns, including capillary columns (Shimadzu instrument).

corresponding acetate (VII) and by its oxidation hexadec-11Z-enal (VIII) were obtained. The yields of the pheromone components (VI-VIII) calculated on the initial cycloalkene were 30, 29.5, and 28%, respectively.



EXPERIMENTAL

The IR spectra of the substances were taken in Nujol on a UR-20 instrument. PMR spectra were recorded on a Tesla BS-567 instrument (100 MHz) with CDCl_3 as solvent and TMS as internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer (22.50 MHz) in CDCl_3 . GLC analysis was conducted on a Chrom-5 instrument with a 3×1200 mm stainless-steel column containing the stationary phase SE-30 (5%) (for compounds (II) and (III)), PEG-20M (15%) [for compound (IV)], or FFAP (for compounds (V), (VI), and (VIII)) on the support Chromaton N-AW-DMCS, with a flame-ionization detector, the carrier gas being helium. The GLC analysis of compounds (II) and (VI) was likewise performed on the Shimadzu instrument using a glass capillary column with dimensions of $0.2 \times 25,000$ mm, the stationary phase being PEG-20M, the working temperature 100°C , and the carrier gas helium. R_f values are given for a fixed layer of Silufol SiO_2 with iodine as the revealing agent.

Methyl 12-oxododecanoate (II) was obtained with a yield of 90% from cyclododecene (I) according to [2].

Methyl Heptadec-12Z-enoate (III). At -30°C , 2.7 g (24.1 mmole) of *t*-BuOK was added in portions to a suspension of 10.0 g (24.1 mmole) of amyltriphenylphosphonium bromide (obtained according to [3]) in 80 ml of absolute THF, and the mixture was stirred at -30°C for 15 min and was then cooled to -78°C and a solution of 3.67 g (16.1 mmole) of the aldehyde (II) in 20 ml of absolute THF was added dropwise. The mixture was stirred at -78°C for 3 h, its temperature was allowed to rise to that of the room over 1.5 h, and it was left for 15 h, after which it was diluted with 800 ml of *n*-hexane, filtered through a layer of SiO_2 and was evaporated, and the residue (3.5 g) was chromatographed on SiO_2 (40/100) with elution by hexane-ether (10:1) to give 2.72 g (60%) of the ester (III), R_f 0.43 [hexane-ether (3:1)], containing none of the *E*- isomer according to GLC.

IR spectrum (ν , cm^{-1}): 3020, 2940, 2870, 1745, 1660, 1475, 1445, 1370, 1275, 1210, 1185, 1135, 1120, 1050, 745. PMR spectrum (δ , ppm): 0.89 (3H, t, $J = 7.5$ Hz, CH_3), 1.29 (20H, m, CH_2), 1.93-2.15 (4H, m, $\text{CH}_2\text{C}=\text{C}$), 2.29 (2H, t, $J = 7.5$ Hz, CH_2CO), 3.65 (3H, s, OCH_3), 5.34 (2H, t, $J = 5$ Hz, $\text{CH}=\text{CH}$). ^{13}C NMR spectrum (δ , ppm): 174.22 (C-1), 34.40 (C-2), 25.0 (C-3), 29.31 (C-4), 29.57 (C-5-C-9), 29.83 (C-10), 26.95 (C-11), 129.83 (C-12, C-13), 27.29 (C-14), 32.05 (C-15), 22.39 (C-16), 14.03 (C-17), 51.37 (c, OCH_3).

Heptadec-12Z-enoic Acid (IV). At 0°C , a solution of 3.57 g of KOH in 37 ml of H_2O was added dropwise to a solution of 0.77 g (2.73 mmole) of the ester (III) in 23 ml of MeOH, and the mixture was heated to $55-60^\circ\text{C}$ and stirred for 7 h and was then left at room temperature for 15 h. It was evaporated, and the residue was extracted with ether (3×30 ml) and was then acidified to pH 2 and was again extracted with ether (4×40 ml). The extract from the acidified solution was dried over MgSO_4 and evaporated. This gave 0.66 g (92%) of the acid (IV), R_f 0.37 [hexane-ether (3:1)].

IR spectrum (ν , cm^{-1}): 3300-3100, 3018, 2940, 2865, 2800-2500, 1712, 1665, 1465, 1420, 1295, 1245, 1135, 1110, 970, 950, 740. PMR spectrum (δ , ppm): 0.89 (3H, t, $J = 6.1$ Hz, CH_3), 1.27 (20H, m, CH_2), 1.93-2.25 (4H, m, $\text{CH}_2\text{C}=\text{C}$), 2.34 (2H, t, $J = 7.5$ Hz, CH_2CO), 5.35 (2H, t, $J = 4.7$ Hz, $\text{CH}=\text{CH}$). ^{13}C NMR spectrum (δ , ppm): 179.72 (C-1), 33.97 (C-2), 24.71 (C-3), 29.04 (C-4), 29.52 (C-5-C-7), 29.42 (C-8), 29.25 (C-9, C-10), 26.92 (C-11), 129.87 (C-12, C-13), 27.20 (C-14), 31.97 (C-15), 22.17 (C-16), 13.98 (C-17).

Hexadec-1,11Z-diene (V). With stirring, 1.58 g of $\text{Pb}(\text{OAc})_4$ was added in portions to a gently boiling mixture of 0.6 g (2.25 mmole) of the acid (IV), 0.052 g of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, 0.13 ml of dry Py, and 5 ml of absolute benzene, and then boiling was continued for 2 h. The reaction mixture was cooled to room temperature, diluted with ether, and filtered through a layer of SiO_2 , which was then washed with ether. The filtrate was washed successively with saturated solutions of NaHCO_3 and NaCl and was dried with MgSO_4 and evaporated. The residue (0.5 g) was chromatographed on SiO_2 (40/100) with elution by n-hexane. This gave 0.36 g (71%) of the diene (V), R_f 0.70.

IR spectrum (ν , cm^{-1}): 3088, 3015, 2935, 2865, 1645, 1470, 1385, 1140, 1120, 1005, 925, 740. PMR spectrum (δ , ppm): 0.89 (3H, t, $J = 6.1$ Hz, CH_3), 1.29 (18H, m, CH_2), 1.92-2.32 (6H, m, $\text{CH}_2\text{C}=\text{C}$), 4.96-5.28 (2H, m, CH_2-1), 5.48 (2H, t, $J = 4.2$ Hz, $\text{CH}=\text{CH}$), 5.83-6.20 (1H, m, H-2). ^{13}C NMR spectrum (δ , ppm): 114.05 (C-1), 139.25 (C-2), 33.86 (C-3), 29.15 (C-4), 29.31 (C-5, C-6), 29.53 (C-7, C-8), 29.75 (C-9), 26.93 (C-10), 129.87 (C-11, C-12), 27.20 (C-13), 31.97 (C-14), 22.38 (C-15), 14.03 (C-16).

Hexadec-11Z-en-1-ol (VI). With stirring, at 0°C , a solution of 0.29 g (2.37 mmole) of 9-BBN in 2.5 ml of absolute THF was added dropwise to a solution of 0.35 g (1.58 mmole) of the diene (V) in 2 ml of the same solvent. The mixture was stirred at room temperature for 5 h and was then cooled to 0°C , and a cooled mixture of 1.92 ml of 3 N NaOH solution and 2.04 ml of 26% H_2O_2 was added dropwise. The resulting reaction mixture was stirred at room temperature for 5 h and was left for 12 h. It was then poured into a cooled solution of sodium bisulfate and was extracted with CH_2Cl_2 (3×30 ml), and the organic extracts were washed successively with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ and with H_2O , dried over MgSO_4 and evaporated. The residue (0.6 g) was chromatographed on SiO_2 (40/100), with elution by a gradient from n-hexane to n-hexane-ether (2:1), giving 0.3 g (80%) of the alcohol (VI) and 0.07 g (20%) of the initial diene (V). According to the results of GLC analysis, the alcohol (VI) contained none of the E- isomer. R_f 0.33 [n-hexane-ether (2:1)]. Its IR and PMR spectra were identical with those described previously [4].

Hexadec-11Z-enyl Acetate (VII). To 0.1 g (0.42 mmole) of the alcohol (VI) was added 2 ml of a 2:3 mixture of acetic anhydride and pyridine and the reaction mixture was stirred at room temperature for 12 h, diluted with diethyl ether (50 ml), washed successively with 5% HCl to give a weak acid medium and with saturated solutions of NaHCO_3 and NaCl , and was dried over MgSO_4 and evaporated. This gave 0.12 g (98%) of the acetate (VII) having IR and PMR spectra identical with those described previously [4].

Hexadec-11Z-enal (VIII). At room temperature, with stirring, a solution of 200 mg (0.83 mmole) of the alcohol (VI) in 0.5 ml of dry CH_2Cl_2 was added in one portion to a suspension of 270 mg (1.25 mmole) of $\text{Py} \cdot \text{CrO}_3 \cdot \text{HCl}$ in 3 ml of the same solvent, and the mixture was stirred for 2 h and was then diluted with 20 ml of diethyl ether and filtered through a small layer of SiO_2 , which was then washed with ether. The filtrate was evaporated, and chromatography of the residue (0.3 g) on SiO_2 (40/100) with elution by hexane-ether (11:1) gave 185 mg (93%) of the aldehyde (VII) having IR and PMR spectra identical with those described previously [5].

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