acetate in a ratio of 1:1. Field trials have shown that the most attractive mixture contains these substances in a ratio of 7.5:92.5.

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INSECT PHEROMONES AND THEIR ANALOGS.

XVII. SYNTHESIS OF (Z)-HEXADEC-11-ENAL AND (Z)-HEXADEC-11-EN-1-YL ACETATE

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(Z)-Hexadec-11-enal and (Z)-hexadec-11-1-yl acetate — components of the sex pheromone of insects of the genera *Heliothis* and *Manestra*, respectively — have been synthesized by the condensation of undec-10-enal with hex-1-yne, deoxygenation of the heptadec-1-en-12-yn-11-ol formed via the corresponding tosylate to heptadec-1-en-12-yne, and the selective oxonolysis of the latter.

(Z)-Hexadec-11-enal and (Z)-hexadec-11-en-1-yl acetate are components of the sex pheromones of many species of insects of the order *Lepidoptera* [1, 2]. The above-mentioned aldehyde has been identified as the main component of these pheromones of moths of the genus *Heliothis* [2-5], and the acetate as a component of the pheromones of moths of the genus *Manestra* [6-8]. These compounds have been synthesized by modifying the carbon skeleton of (Z)-unsaturated compounds [9] by Wittig's method for the olefination of carbonyl compounds [10-12], or via the corresponding alkynes obtained by the interaction of alkali-metal acetylides with alkyl halides [8, 13-16] (see following page).

We have found a route to the synthesis of the hexadec-11-enal (VII) and the hexadec-11-en-1-yl acetate (X) with the (Z)-configuration that is based on the interaction of the readily available undec-10-enal (I) with hex-1-yn-1-ylmagnesium bromide. The deoxygenation of the heptadec-1-en-12-yn-11-ol (II) so formed via the corresponding tosylate (III) gave the key synthon — heptadec-1-en-12-yne (IV). As was to be expected, the ozonolysis of the enyne (IV) took place selectively at the double bond and, depending on the subsequent treatment of the peroxide product of ozonolysis, led either to 1,1-dimethoxyhexadec-11-yne (V) or to hexadec-11-yn-1-ol (VIII). The acetylenic acetal (V) was smoothly converted into the desired (Z)-alkenic aldehyde (VII) by hydrogenation over Lindlar catalyst in the presence of quinoline to 1,1-dimethoxyhexadec-11Z-ene (VI) followed by the elimination of the acetyl protection in an acid medium. To convert the acetylenic alcohol (VIII) into the other desired product —

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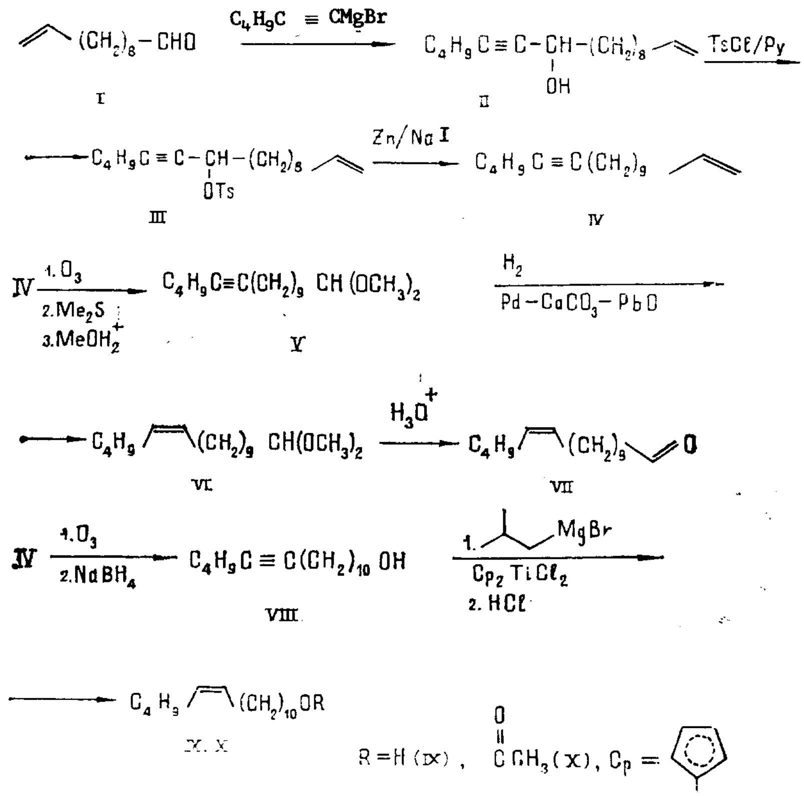

the (Z)-alkenic acetate (X) — it was most rational to use the reductive Grignardization reaction [17]. The yields of these pheromones (VII) and (X) in the syntheses mentioned amounted to 20 and 25%, respectively, based on the initial aldehyde (I).

According to the results of GLC analysis in a capillary column, the stereopurity of compounds (VII) and (X) was not less than 95%. It must be mentioned that the aldehyde (VII) contained about 3% of the corresponding saturated compound.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film) and PMR spectra on a Tesla BS-497 spectrometer at a working frequency of 100 MHz using CDl_3 as the solvent; chemical shifts are given on the δ scale relative to the signal of TMS (internal standard). The mass spectrum was measured on a MKh-1306 instrument at a temperature of the ionization chamber of 140°C and with an ionizing energy of 70 eV. GLC analysis was performed on a Chrom-5 instrument with, as the stationary phase, the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at working temperatures of 50-300°C with helium as the carrier gas. The GLC analysis of compounds (VII) and (X) was performed on the Chrom-5 instrument with a stainless-steel capillary column (0.25 mm × 50 m), the stationary phase being 1,2,3-tris-(β-cyanoethoxy)-propane, the working temperature 140-145°C, and the carrier gas helium.

Heptadec-1-en-12-yn-11-ol (II). To 20 ml of a 0.75 M solution of ethylmagnesium bromide in diethyl ether was added 1.5 g (18 mmole) of hex-1-yne and the mixture was boiled for 3.5 h and was then cooled to 0°C, and 1.2 g (7 mole) of the aldehyde (I) in 5 ml of absolute ether was added dropwise. The reaction mixture was stirred at 0-2°C for 4 h and then 40 ml of saturated NH_4Cl was added and it was kept at 20°C for 0.5 h, after which 300 ml of diethyl ether was added and the organic layer was separated off, washed with saturated NaCl, dried with Na_2SO_4, and evaporated. This gave 1.5 g (85% of compound (II), n_D^{20} 1.4665. IR spectrum (ν, cm^{-1}) 910 s, 990 s, 1030 m, 1645 nm, 3235 w, 3100 m, 3200-3600 br.s. PMR spectrum (δ, ppm): 0.9 t (3 H, CH_3, J = 6.5 Hz) 1.2-1.7 m (18 H, CH_2), 1.9-2.3 m (4 H, $CH_2C=C$, $CH_2C\equiv C$), 4.34 t (1 H, OCH, J = 5 Hz, 4.85-5.15 m (2 H, $CH_2=C$), 5.65-6.0 m (1 H, CH = CH). Calculated, %: C 81.49, H 12.04. $C_{17}H_{30}O$. Found, %: C 81.53, H 12.08.

11-Tosyloxyheptadec-1-en-12-yne (III). At −50°C 1.4 g (7.3)mmole) of p-toluenesulfonyl chloride was added in portions to a solution of 1.5 g (6 mmole) of the alcohol (II) in 2.2 ml of dry pyridine and the mixture was stirred at −5°C for 6 h and was kept at 0°C for 12 h, after which it was poured onto ice (10 g) and extracted with diethyl ether (300 ml). The ethereal solution was washed successively with 10% HCl (to pH 4), with 10% $NaHCO_3$ (to pH 8), and with saturated NaCl (to pH 7) and was dried with $MgSO_4$ and evaporated. This gave 1.92 g (79%) of the tosylate (III). IR spectrum (ν, cm^{-1}): 580 s, 660 m, 918 m, 1010 w, 1596 m, 1642 m, 3083 w.

Pentadec-1-en-12-yne (IV). A mixture of 1.5 g (3.7 mmole) of the tosylate (III), 3 g (20 mmole) of sodium iodide, and 12.8 g (195 mg-atoms) of zinc dust in 72 ml of absolute THF was stirred vigorously (65-70°C for 3 h, and 20°C for 3 h; Ar) and then the reaction mixture was filtered, diluted with diethyl ether, washed with ether, and with saturated $NaHCO_3$, dried with $MgSO_4$, and evaporated. The residue was chromatographed (neutral Al_2O_3 hexame). This gave 0.46 g (53%) of compound (IV), n_D^{20} 1.4535.

IR spectrum (ν, cm^{-1}): 730 m, 920 s, 1000 m, 1642 m, 3085 m. PMR spectrum (δ, ppm): 0.89 t (3 H, CH_3, j = 6 Hz), 1.16-1.58 m (18 H, CH_2), 1.98-2.3 m (6 H, $CH_2C = C$, $CH_2C \equiv C$), 4.87-5.07 m (2 H, $CH_2 = C$), 5.6-5.95 m (1 H, CH = C). Calculated, %: C 87.04, H 12.88. $C_{17}H_{30}$. Found, %: C 87.10, H 12.90. Mass spectrum ([m/z (J, %)]: M^+ 234 (0.16), $[M - 15]^+$ 219 (0.16, $[M - C_3H_7]^+$ 191 (1.0), 149 (3.26), 135 (4.47), 121 (6.32), 109 (7.89), 107 (6.05), 95 (42.11), $[C_4H_9C \equiv C]^+$, 81 (71.05), 57 (31.58), 43 (22.63), $[C_3H_5]^+$ 41 (100%).

1,2-Dimethoxyhexadec-11-yne (V). A mixture of ozone and oxygen (2 wt.% of O_3) was passed at the rate of 5 liters/hour thorugh a solution of 0.35 g (1.5 mmole) of the enzyme (IV) in 5ml of cyclohexane until 1.5 mmole of ozone had been absorbed. The reaction mixture was purged with argon and was diluted with 3 ml of ethanol, after which 0.55 ml of dimethyl sulfide was added to it at 5°C and, after being stirred for 6 h, it was kept at room temperature until the peroxide had disappeared (test with acidified aqueous KI solution) (15 h) and was evaporated under reduced pressure; the residue was dissolved in 100 ml of diethyl ether and the solution was washed with water (3 × 10 ml) and was dried with $MgSO_4$. The residue after evaporation was dissolved in 15 ml of absolute methanol, 0.04 g of p-toluene sulfonic acid was added, and the mixture was stirred at 20°C for 36 h and was then treated with 0.2 g of solid $NaHCO_3$ and was evaporated. The residue was dissolved in 100 ml of diethyl ether and the solution was washed with 10 ml of saturated $NaHCO_3$, and dried with Na_2SO_4, and evaporated. The new residue was chromatographed on SiO_2 [hexane—diethyl ether (15:1)]. This gave 0.32 g (75%) of compound (V), n_D^{20} 1.4498.

IR spectrum (ν, cm^{-1}): 1065 m, 1080 m, 1132 s, 2245 w, 2380 w. PMR spectrum (δ, ppm): 0.9 t (3 H, CH_3, J = 6 Hz), 1.18-1.65 m (20 H, CH_2), 2.15 m (4 H, $CH_2C \equiv C$), 3.31 s (6 H, OCH_3), 4.36 t (1 H, OCHO, J = 5.5 Hz). Calculated, %: C 76.49, H 12.11. $C_{18}H_{34}O_2$. Found, %: C 76.54, H 12.13.

1,1-Dimethoxyhexadec-11Z-ene (VI). A solution of 0.25 g (0.9 mmole) of the acetal (V) in 5 ml of absolute n-hexane was treated with 0.01 g of quinoline and 0.03 g of Lindlar catalyst. The mixture was cooled to 10°C and hydrogenation was carried out at an atmospheric pressure until 20 ml of hydrogen had been absorbed (0.5 h). Then the catalyst was filtered off, and the filtrate was diluted with 50 ml of diethyl ether, washed with 5% HCl and with saturated NaCl, and was dried with $MgSO_4$. Evaporation gave 0.23 g (92%) of compound (VI), n_D^{20} 14480.

IR spectrum (ν, cm^{-1}): 730 w, 970 w, 1065 m, 1085 m, 1132 s, 3010 m. PMR spectrum (δ, ppm): 0.9 t, (3 H, CH_3, J = 6.5 Hz), 1.15-1.5 m (20 H, CH_2), 1.88-2.15 m (4 H, $CH_2C = C$), 3.31 s (6 H, OCH_3), 4.35 t (1 H, OCHO, J = 5.5 Hz), 5.36 t (2 H, CH = CH, J = 5 Hz), Calculated, %: C 75.95, H 12.73. $C_{18}H_{36}O_2$. Found, %: C 75.99, H 12.76.

Hexadec-11Z-enal (VII). A solution of 0.14 g (0.5 mmole) of the acetal (VI) in 6 ml of acetone was treated with 0.15 ml of water and 0.04 g of pyridinium tosylate and was boiled (Ar; 2.5 h). Then the reaction mixture was evaporated and the residue was dissolved in 100 ml of diethyl ether; the solution was washed successively with saturated solutions of NH_4Cl, of $NaHCO_3$, and of NaCl, and was dried with $MgSO_4$ and evaporated. After chromatography [SiO_2, hexane—diethyl ether (15:1)], 0.1 g (83%) of the aldehyde (VII) was obtained with n_D^{20} 1.4552, its IR and PMR spectra being identical with those described in the literature [18].

Hexadec-11-yn-1-ol (VIII). At 5°C a mixture of ozone and oxygen (2 wt.% of O_3) was passed at the rate of 5 liters/h through a solution of 0.35 g (1.5 mmole) of the enzyme (IV) in 5 ml of cyclohexane containing 0.15 ml of absolute methanol until 1.5 mmole of ozone had been absorbed. The reaction mixture was purged with argon, and, at 10°C, 3 ml of methanol and 0.09 g (2.4 mmole) of sodium tetrahydroborate were added and the mixture was kept at room temperature for 15 h, then 1 ml of a 10:1 mixture of water and acetic acid was added, the mixture was stirred at 20°C for 1 h and was evaporated under reduced pressure, and the residue was dissolved in 100 ml of diethyl ether, this solution then being washed with saturated $NaCO_3$, dried with Na_2SO_4, and evaporated. After chromatography [SiO_2, hexane—diethyl ether (7:3)], 0.3 g (85%) of compound (VIII) was obtained with n_D^{20} 1.4657, its IR and PMR spectra being identical with the spectra described in the literature.

Hexadec-11Z-en-1-ol (IX). At 0°C, 3.5 ml (4.9 mmole) of a 1.4 M solution of isobutylmagnesium bromide in diethyl ether was added to a solution of 0.24 g (1 mmole) of the alkynol (VIII) in 10 ml of absolute diethyl ether and the mixture was stirred for 15 min and was then warmed to room temperature, after which 0.015 g of Cp_2TiCl_2 was added and stirring was continued until the evolution of gas had ceased (1-1.5 h). The reaction mixture was cooled to 0°C and 5 ml of 10% HCl was added, and it was then stirred at 20°C for 0.5 h and, after the addition of 100 ml of diethyl ether, the organic layer was separated off and was washed successively with saturated solutions of NaCl and $NaHCO_3$, dried with Na_2SO_4, filtered through a layer (5 cm) of Al_2O_3, and evaporated. This gave 0.22 g (92%) of compound (IX) with n_D^{20} 1.4598 (see [15, 16]). The IR and PMR spectra were identical with those described in the literature [15].

Hexadec-11Z-en-1-yl Acetate (X). The acetate (X) was obtained in the usual way from 0.18 g (0.75 mmole) of the alkenol (IX), 0.8 ml of pyridine, and 0.5 ml of acetic anhydride; its yield after chromatography on [SiO_2 (hexane—diethyl ether (15:1)] was 0.19 g (90%, n_D^{20} 1.4514, its IR and PMR spectra being identical with the spectra described in the literature [15].

SUMMARY

Hexadec-11Z-enal and hexadec-11Z-en-1-yl acetate — components of the sex pheromones of the genera *Heliothis* and *Mamestra*, respectively — have been synthesized by the condensation of undec-10-enal with hex-1-yne and selective ozonolysis of the intermediate heptadec-1-en-12-yne.

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