

PHEROMONES OF INSECTS AND THEIR ANALOGS

XXXIII. SYNTHESIS OF HEXADEC-7Z,11E-DIEN-1-YL ACETATE - THE SEX PHEROMONE OF *Sitotroga cerealella* AND A COMPONENT OF THE SEX PHEROMONE OF *Pectinophora gossypiella*

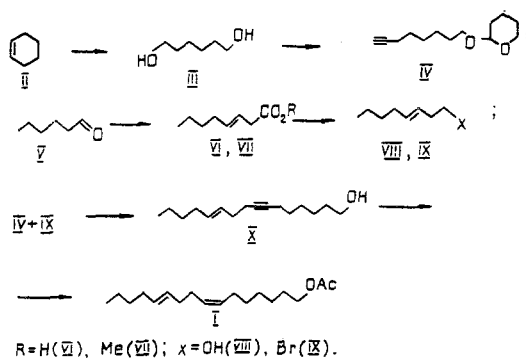
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From cyclohexene and caproaldehyde, using ozonolysis and the Knoevenagel reaction, we have synthesized hexadeca-7Z,11E-dien-1-yl acetate - the sex pheromone of *Sitotroga cerealella* and a component of the sex pheromone of *Pectinophora gossypiella*.

Hexadeca-7Z,11E-dien-1-yl acetate (I) - the sex pheromone of the Angoumois grain moth *Sitotroga cerealella* [1] and a component of the sex pheromone of the pink bollworm *Pectinophora gossypiella* [2, 3] - has been synthesized previously with the aid of the Wittig reaction [4, 9] or via acetylene derivatives [3-5, 9-12].

According to a scheme that has been developed, one of the synthons for pheromone (I) [1-(2-tetrahydropyranyloxy)oct-7-yne (IV)] was obtained by the ozonolysis of cyclohexene (II) followed by the selective transformation [10] of the ozonolysis product - hexane-1,6-diol (III). By a modified [13] Knoevenagel reaction, caproaldehyde (V) was converted into the alk-3E-enoic acid (VI), the esterification of which and reduction of the methyl ester (VII) with the aid of diisobutylaluminum hydride (DIBAH) gave oct-3E-en-1-ol (VIII). Treatment of the latter with triphenylphosphine dibromide led to the homoallyl bromide (IX). The coupling of synthons (IV) and (IX) took place most smoothly under the action of lithium amide in liquid ammonia containing DMSO and THF and, after acid treatment, led to the enynic precursor (X), the Z-selective hydrogenation of which, followed by acetylation gave the desired pheromone (I). The overall yield of (I) in this convergent synthesis amounted to 20% calculated on the cyclene (II) or 23% on the aldehyde (V).



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film), PMR spectra were recorded on a Tesla BS-567 instrument (working frequency 100 MHz); and <sup>13</sup>C NMR spectra were taken on a Jeol FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression of proton coupling, the solvent being CDCl<sub>3</sub>. Chemical shifts are given on the δ scale relative to the

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signal of TMS (internal standard). GLC analysis of compounds (III), (IV), (VII)-(IX) was conducted on a Chrom-5 instrument with, as stationary phase, the silicone liquid SE-30 (5%) on Chromaton NAW-DMCS (0.16-0.2 mm) at a working temperature of 50-300°C; for compounds (I) and (X) a Shimadzu instrument was used with the stationary phase PEG-20M in a glass capillary column with dimensions of 0.2 mm × 25 m at working temperatures of 160 and 180°C, respectively, the carrier gas being helium.

Hexane-1,6-diol (III). An ozone-oxygen mixture (5.5 wt. % of O<sub>3</sub>) was passed at the rate of 20 liters/h through a solution of 8.2 g (0.1 mole) of cyclohexene (II) in 125 ml of cyclohexane containing 20 ml of absolute methanol at 5°C until 4.8 g (0.1 mole) of ozone had been absorbed. The reaction mixture was purged with argon, the solvent was decanted off, and the residual peroxide product was dissolved in 100 ml of methanol; the solution was cooled to 15°C and 9.5 g (0.25 mole) of NaBH<sub>4</sub> was added in portions, after which the reaction mixture was stirred at room temperature for 15 h and was then treated with 33 ml of water-acetic acid (10:1) and after being stirred for 3 h it was filtered, the filtrate was evaporated, the residue was extracted with diethyl ether (3 × 300 ml), and the extract was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. This gave 8.87 g (75%) of the diol (III), mp 42-43°C [14].

1-(2-Tetrahydropyranyloxy)oct-7-yne (IV). As described in [10], 5.9 g (0.05 mole) of the diol (III) yielded 5.9 g (56%) of compound (IV), the IR and PMR spectra of which were identical with those given in [10].

Methyl Oct-3E-enoate (VII). To 21.9 g (0.154 mole) of oct-3-enoic acid (VI) obtained from hexanal (V) according to [13] were added 0.24 g of TsOH and 215 ml of absolute methanol, the mixture was kept at room temperature for 24 h, and the solvent was distilled off and the residue was dissolved in 300 ml of ethyl ether; the solution was washed successively with saturated solutions of NaHCO<sub>3</sub> and NaCl was dried with MgSO<sub>4</sub> and evaporated, and the residue was distilled to give 21.4 g (89%) of the ester (VII), n<sub>D</sub><sup>20</sup> 1.4461, bp 69-72°C (10 mm) [15]. IR spectra (ν, cm<sup>-1</sup>): 985 (C=C-H), 1265 (C-O-C), 1660 (C=C), 1740 (C=O). PMR spectrum (100 MHz, CDCl<sub>3</sub>): 0.89 (t, 3H, J = 6.7 Hz, H-8), 1.2-1.54 (m, 4H, H-6, H-7), 1.96-2.26 (m, 2H, H-5), 3.04 (d, 2H, J = 4.5 Hz, H-2), 3.68 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 5.51-5.68 (m, 2H, H-3, H-4).

Oct-3E-en-1-ol (VIII). A solution of 11.0 g (70.5·10<sup>-3</sup> mole) of the ester (VII) in 210 ml of absolute diethyl ether was treated (Ar, -20°C) with 66.0 ml of a 73% solution of DIBAH (0.291 mole) in toluene, and the mixture was stirred for 2 h and was then heated to 0°C and, after the dropwise addition of 70 ml of water, it was stirred at room temperature for 2 h and was extracted with ethyl ether (2 × 200 ml). The combined extracts were washed with saturated NaCl solution, dried with MgSO<sub>4</sub>, and evaporated to give 8.39 g (93%) of the alcohol (VIII), n<sub>D</sub><sup>20</sup> 1.4460. Its IR and PMR spectra were identical with those described in the literature [11].

1-Bromooct-3-ene (IX). A solution of 3.0 ml (58.2·10<sup>-3</sup> mole) of bromine in 5 ml of absolute CCl<sub>4</sub> was added dropwise to a suspension of 15.27 g (58.3·10<sup>-3</sup> mole) of triphenylphosphine in 70 ml of absolute CCl<sub>4</sub> at 15°C, the mixture was stirred at room temperature for 0.5 h and was then cooled to 15°C, and 7.4 g (57.8·10<sup>-3</sup> mole) of the alcohol (VIII) in 10 ml of absolute CCl<sub>4</sub> was added, and the resulting reaction mixture was stirred at room temperature for 1 h and was then filtered, the filtrate was evaporated, and the residue was chromatographed (SiO<sub>2</sub>, hexane) to give 9.17 (83%) of the bromide (IX), n<sub>D</sub><sup>20</sup> 1.4698. Its IR and PMR spectra were identical with those described in [11].

Hexadec-11E-en-7-yn-1-ol (X). A solution of 2.73 g (13.0·10<sup>-3</sup> mole) of 1-(2-tetrahydropyranyloxy)oct-7-yne (IV) in 5 ml of absolute THF was added to a suspension of lithium amide obtained from 0.11 g (15.7·10<sup>-3</sup> g-atom) of lithium, 0.02 g of ferric chloride, and 60 ml of redistilled liquid ammonia, and the mixture was stirred for 1 h; then 2.5 g (13.0·10<sup>-3</sup> mole) of the bromide (IX) and, immediately after this, 5 ml of absolute DMSO were added and the resulting mixture was stirred at -35°C for 3 h and was then allowed to warm up to room temperature over 2 h with the complete evaporation of the ammonia, after which 30 ml of water was added, extraction was carried out with hexane (3 × 100 ml), and the combined extracts were washed successively with 10% HCl, and saturated solutions of NaHCO<sub>3</sub> and NaCl and were evaporated.

The residue was dissolved in 30 ml of methanol, and 0.3 g of TsOH and 3 ml of water were added and the mixture was stirred at room temperature for 24 h, after which it was evaporated and the residue was dissolved in 200 ml of diethyl ether; this solution was washed

successively with saturated solutions of  $\text{NaHCO}_3$  and  $\text{NaCl}$  and was dried with  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was chromatographed [ $\text{SiO}_2$ , hexane-diethyl ether (7:3)], to give 1.87 g (61%) of the alcohol (X) containing, according to capillary GLC, not less than 98% of the main substance,  $n_D^{20}$  1.4745. Its IR and PMR spectra were identical with those given in [12].  $^{13}\text{C}$  NMR spectrum (22.5 MHz,  $\text{CDCl}_3$ ): 62.94 (t, C-1), 32.68 (t, C-2), 25.27 (t, C-3), 29.04 (t, C-4), 28.56 (t, C-5), 18.68 (t, C-6), 79.88 (s, C-7), 80.36 (s, C-8), 19.33 (t, C-9), 32.21 (t, C-10), 128.52 (d, C-11), 131.60 (d, C-12), 32.34 (t, C-13), 32.68 (t, C-14), 22.15 (t, C-15), 13.91 (q, C-16).

Hexadeca-7Z,11E-en-1-yl Acetate (I). With stirring, a solution of 0.04 g ( $1.05 \cdot 10^{-3}$  mole) of sodium tetrahydroborate in 2 ml of ethanol, and then 0.08 ml of ethylenediamine, and, after this, 0.6 g ( $2.5 \cdot 10^{-3}$  mole) of the enynic alcohol (X) were added to a solution of 0.162 g ( $0.65 \cdot 10^{-3}$  mole) of nickel acetate in 2 ml of 95% ethanol, and hydrogenation was carried out at room temperature. After the end of hydrogenation (monitoring with the aid of TLC), the reaction mixture was filtered, the solvent was distilled off, the residue was dissolved in 100 ml of diethyl ether, and this solution was washed successively with 10% HCl and a saturated solution of  $\text{NaCl}$  and was dried with  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was treated with 3 ml of acetic anhydride-pyridine (2:3), the mixture was kept at room temperature for 24 h, and it was then diluted with 100 ml of methylene chloride and was washed successively with 10% HCl and saturated solutions of  $\text{NaHCO}_3$  and  $\text{NaCl}$  and was dried with  $\text{MgSO}_4$  and evaporated. The residue was chromatographed [ $\text{SiO}_2$ , hexane-diethyl ether (9:1)] to give 0.55 g (78%) of the acetate (I) containing, according to capillary GLC, not less than 96% of the main substance,  $n_D^{20}$  1.4605. Its IR and PMR spectra were identical with those given in [12].  $^{13}\text{C}$  NMR spectrum (22.5 MHz,  $\text{CDCl}_3$ ): 64.63 (t, C-1), 32.73 (t, C-2), 25.84 (t, C-3), 28.93 (t, C-4), 28.61 (t, C-5), 27.47 (t, C-6), 129.65 (d, C-7), 129.38 (d, C-8), 27.20 (t, C-9), 29.58 (t, C-10), 129.93 (d, C-11), 130.79 (d, C-12), 32.29 (t, C-13), 31.80 (t, C-14), 22.21 (t, C-15), 13.98 (q, C-16), 171.21 (s, OAc).

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