INSECT PHEROMONES AND THEIR ANALOGUES.

X. THE STEREODIRECTED SYNTHESIS OF (E,E)-DODECA-8,10-DIENOL

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A passage from deca-1,4,9-triene (I) to (E,E)-dodeca-8,10-dienol (II) in five stages with an overall yield of 23% has been found by the selective transformations of deca-1,4,9-trien-1-yltrimethylsilane. Thus, under mild conditions, by the hydrogenation of (I) with the aid of 9-borabicyclo[3.3.1]nonane (9-BBN) followed by oxidation with H_2O_2 (E,E)-deca-6,8-dienol was obtained with a yield of 60%, and this was converted quantitatively into the corresponding tosylate. The ethynylation of the latter with lithium acetylide gave (E,E)-dodecadien-1-yne (III) on a Lindlar catalyst followed by the reaction of the resulting triene with 9-BBN, as described above for (I) led to the desired codlemone (II). The IR, PMR, ^{13}C NMR, UV, and mass spectra of the compound obtained are discussed.

The majority of known methods for the synthesis of the sex pheromone of the codling moth *Laspeyrsia pomonella* [1] are based on the use of sorbic acid derivatives contained a preformed (E,E)-system [2-8]. The dienic hydrocarbon piperylene, in the form of the irontricarbonyl complex, has been rearranged to the carbon skeleton of the pheromone by condensation with 7-ethoxycarbonylpentanoyl chloride [9]. The construction of the conjugated diene system with the aid of the Wittig reaction does not take place stereospecifically [10]. The ratio of the (E,E)- and (Z,E)- isomers amounts to 78:22 in the decarboxylation of the adduct of the corresponding enal and the carboxylate of the enolate [11]. In syntheses using the stereospecific opening of the ring in cyclopropane carbinols [12] or the thermolysis of allyl sulfoxides [13] selectivity for the (E,E)- isomer reached 90%. A method of synthesizing this pheromone based on a co-oligomer of butadiene with methyl acrylate has also been proposed [14, 15].

We have developed a new route for the stereodirected synthesis of the sex hormone of the codling moth (codlemone), which is based on selective transformations of deca-1,4,9-trien-1-yltrimethylsilane (I), an accessible polymer of butadiene and trimethylvinylsilane, which is smoothly desilylated under the action of potassium tert-butanolate in hexametapol with an almost quantitative yield of (E,E)-deca-1,6,8-triene (II) [16]. The formation of the latter by the co-oligomerization of butadiene with ethylene [17] and subsequent isomerization of the decatriene with potassium tert-butanolate in dimethyl sulfoxide [18] or by an alkali-metal hydroxide deposited on alumina [19] takes place with a far lower selectivity.

The hydroboration of the triene (II) with the aid of 9-borabicyclo[3.3.3]nonane (9-BBN) under mild conditions took place exclusively at the terminal double bond. Subsequent oxidation of the organoboron intermediate by alkaline hydrogen peroxide led with a yield of about 60% to the (E,E)-deca-6,8-dienol (III). The ^{13}C NMR spectrum of the dienol (III) showed the signals of the C_{10} and C_5 atoms at 18.01 ppm (quartet) and 32.51 ppm (triplet), which corresponds to literature information [23] for conjugated (E,E)-dienic hydrocarbons and thus confirms the (E,E)-configuration of compound (III).

The dienol (III) was then converted quantitatively under the action of tosyl chloride into the corresponding tosylate (IV). When the latter was condensed with lithium acetylide the previously undescribed (E,E)-dodeca-8,10-dien-1-yne (V) was obtained with a yield of more than 80%. The absorption maximum in the 229 nm region (ε 22,400) of the UV spectrum

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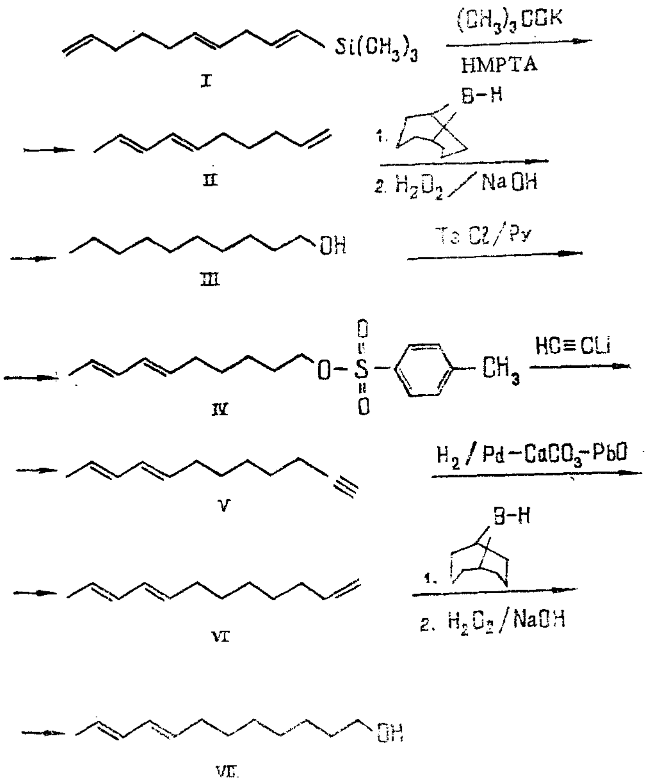
[20], and also the narrow intense peak (990 cm^{-1}) in the IR spectrum [12, 21] confirmed the presence of a conjugated (E,E)-dienic system in compound (V). The PMR spectrum of this compound contained a multiplet in the 5.4-6.4 ppm region with a microstructure identical to the multiplet of the protons of the conjugate diene systems of the known compounds (II) and (III), although the multiplet of the dienyne (V) was shifted downfield by 0.2-0.3 ppm.

The mass spectrum of compound (V) contained the corresponding molecular ions (M^+ 162) for which fragmentation at the α- and β-carbon-carbon bonds in relation to the dienic system and the ethynyl group is characteristic.



The dienyne (V) was selectively hydrogenated on a Lindlar catalyst, being quantitatively converted into (E,E)-dodeca-1,8,10-triene (VI). The IR and UV spectra of this compound were similar to the spectra of the decatriene (II). However, in the PMR spectra of the trienes (II) and (VI) there were appreciable differences caused by the substantially greater mutual influence of the two unsaturated systems in the triene (II) with a shorter hydrocarbon chain. The spatial orientation of the dienic and enic systems in relation to one another is apparently such that they prove to be in a region of increased screening, i.e., above or below the plane of the double bonds. A consequence of this is an upfield shift both of the multiplet of the protons of the conjugated system (by 0.2 ppm) and an even more substantial shift of the protons of the vinyl group (by 0.5 ppm) of triene (II) as compared with the longer chain triene (VI).

The selective hydroboration of triene (VI) with an equimolar amount of 9-BBN followed by oxidation led with a yield of 58% to the desired (E,E)-dodeca-8,10-dienol (VII) (scheme). Characteristic for the mass spectra of both dienic alcohols (III) and (VII) is the fragmentation of the corresponding M^+ ions at the C—C bond in the allyl position with the formation of the ion $C_6H_9^+$ (m/z 81), having the maximum intensity. The over-all yield of codlemone in this six-stage synthesis amounted to 23% calculated on the initial co-oligomer (I).

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer in a thin layer. UV spectra were taken on a Specord UV-VIS instrument in hexane as solvent. PMR spectra were obtained on a Tesla BS-467 spectrometer with a working frequency of 60 MHz with $CDCl_3$ and CCl_4 as solvents, the chemical shifts being given in the δ scale relative to the signal of TMS (internal standard). The ^{13}C NMR spectra of compound (III) in the form of a 20% solution in $CDCl_3$ was obtained on a JEOL FX-90 Q spectrometer (22.5 MHz) with broad-band suppression in relation to protons in the monoresonance regime with partial retention of the Overhauser effect. TMS was used as an internal standard. Mass spectra were taken on MKh-1306 instrument at a temperature of the ionization chamber of 120°C and an ionizing voltage of 70 V. GLC analysis was performed on a Chrom-5 instrument with a flame-ionization detector using as stationary phase 1,2,3-tris(β-cyanoethoxy)propane (10%) on Chromosorb G-AW-DMCS (0.2 mm) modified with $AgNO_3$ (2%); column 2.5 m × 3 mm, temperature 145°C, carrier gas helium.

The Deca-1,6,8-triene (II). To a solution of 7.84 g (0.07 mole) of potassium tert-butanolate in 5 ml of hexametapol was added 31.2 g (0.15 mole) of the silane (I). The mixture was kept at 60°C for 3 h and was then cooled and washed with several portions of water to neutrality. The upper layer was separated off and distilled. This gave 19.3 g (94.9%) of the decatriene (II) with bp 49-51°C (9 mm), n_D^{20} 1.4491 [16]. UV spectrum (λ_{max}): 229 nm (ε 10,600). PMR spectrum (ppm): 1.4 (2 H, CH_2, m), 1.65 (3 H, CH_3—C=C, J = 6 Hz, d), 1.8-2.4 (4 H, 2 CH_2—C=C, m), 4.7-5.15 (4.72, 4.98, 5.07) (3 H, CH=CH_2, m), 5.25-6.2 (4 H, CH=CH—CH=CH, m).

(E,E)-Deca-6,9-dienol (III). At 0°C, with stirring, 200 ml of a 0.5 M solution of 9-BBN in absolute THF was added to a solution of 13.6 g (0.1 mole) of the decatriene (II) in 15 ml of absolute THF. The mixture was stirred at 20°C for 2 h and was cooled to 0°C, and a cooled mixture of 80 ml of a 3 M solution of NaOH and 80 ml of 30% H_2O_2 were added dropwise. After this, the mixture was stirred at 20°C for 3 h and then 500 ml of diethyl ether was added, the organic layer was separated off and was washed with saturated NaCl solution, dried over Na_2SO_4, and evaporated. The residue was distilled in vacuum, giving 9.2 g (60%) of the alcohol (III), bp 108-110°C (8 mm), n_D^{20} 1.4872. IR spectrum (ν, cm^{-1}): 995 s, 1060 s, 3025 m, 3400 br.s.. UV spectrum (λ_{max}): 229 nm (20,950). PMR spectrum (ppm): 1.37 (6 H, CH_2, m), 1.68 (3 H, CH_3—C=C, J = 6 Hz, d), 2.02 (2 H, CH_2—C=V, m), 3.5 (2 H, CH_2O, J = 6 Hz, t), 5.2-6.2 (4H, 2 × CH=CH, m). ^{13}C NMR spectrum (ppm); 18.01 (C_{10}, q), 25.31 (C_3, t), 29.24 (C_4, t), 32.51 (C_5, t), 32.61 (C_2, t), 62.81 (C_1, t), 126.80 (C_7, d), 130.44 (C_8, d), 131.65 (C_9, d), 131.74 (C_6, d). Mass spectrum (m/z (I, %)): 154 M^+ (20.8), 152 (M^+ — 2H), (3.8), 136 (M^+ — H_2O) (3.3), 121 (M^+ — 33), (7.9), 107 (16.3), 93 (23.3), 81 (100), 68 (98.9), 55 (66.7). Found, %: C 77.92; H 11.75. $C_{10}H_{18}O$. Calculated, %: C 77.86; H 11.76.

(E,E)-1-Tosyloxydeca-6,8-diene (IV). At —5 to 0°C, 12.7 g (0.06 mole) of p-toluenesulfonyl chloride was added in portions to a solution of 9.2 g (0.06 mole) of the alcohol (III) in 20 ml of dry pyridine. The mixture was stirred at —5°C for 0.5 h and was then kept at 0°C for 6 h and was poured onto ice and extracted with diethyl ether. The ethereal solution was washed with 10% HCl to pH 4 and then with 10% $NaHCO_3$ and with saturated NaCl solution and was dried with Na_2SO_4 and evaporated. This gave 17.5 g (95%) of the tosylate (IV). IR spectra (ν, cm^{-1}): 560 s, 575 s, 668 s, 820 m, 910 m, 960 m, 998 m, 1180 s, 1605 w-m. Found %: C 66.30; H 7.77; S 10.11. $C_{17}H_{24}O_3$. Calculated %: C 66.24; H 7.79; S 10.40.

(E,E)-Dodeca-8,10-dien-1-yne (V). At 0-5°C, 15.4 g (0.05 mole) of the tosylate (IV) in 30 ml of absolute THF was added to a solution in 90 ml of dry hexametapol of the lithium acetylide obtained from 0.76 g (0.11 g-atom) of lithium in 200 ml of liquid ammonia followed by the evaporation of the ammonia. The mixture was stirred at 0-5°C for 10 h and then 50 ml of water was added, stirring was continued at 20°C for 1 h, and the mixture was extracted with pentane (3 × 300 ml). The organic layer was washed with water (2 × 100 ml), dried over Na_2SO_4, and evaporated. The residue was charomatographed on silica gel (with hexane as the eluent) giving 6.6 g (82%) of the dienyne (V), n_D^{20} 1.4865. IR spectrum (ν, cm^{-1}): 990 s, 2255 w, 2380 w, 3320 m. UV spectrum (λ_{max}): 229 nm (ε 18,300). PMR spectrum (ppm): 1.47 6 H, 3 × CH_2, m), 1.73 (2 H, CH_2C≡C, J = 2.5 Hz, t), 1.72 (3 H, CH_3C=C, J = 6 Hz, d), 2.13 (3 H, CH_2C=C, C≡CH, m), 5.4-6.4 (5.78, 5.88, 5.98, 6.05, 6.3) (4 H, CH=CH—CH=CH, m). Mass spectrum (m/z) (I, %)): 162 M^+ (16.3), 161 (M^+ — 1) (10.6), 148 (30.1), 147 (34.15), 134 (49.6), 133 (32.5), 120 (82.1), 199 (38.2), 105 (77.2), 91 (45), 80 (78.9), 67 (56.9), 54 (64.2), 41 (100). Found, %: C 88.96; H 11.04. $C_{12}H_{18}$. Calculated, %: C 88.90; H 11.10.

(E,E)-Dodeca-1,8,10-triene (VI). The solution of 1.61 g (0.01 mole) of compound (V) in 20 ml of hexane was treated with 0.25 g of Lindlar catalyst and 0.1 g of quinoline, and hydrogenation was carried out at atmospheric pressure until 225 ml (0.01 mole) of hydrogen had been absorbed (2-3 h). The reaction mixture was diluted with 80 ml of diethyl ether, the catalyst was filtered off, and the filtrate was washed with 10% HCl and then with saturated NaCl solution, and it was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (with hexane as eluent), giving 1.56 g (95%) of the triene (VI), n_D^{20} 1.4830. IR spectrum (ν, cm^{-1}): 620 s, 990 s, 1640 m, 3020 m, 3080 w. UV spectrum (λ_{max}): 229 (ε 17,200). PMR spectrum (ppm): 1.37 (6 H, 3 × CH_2, m), 1.63 (3 H, $CH_3C{=}C$, J = 6 Hz, d), 2.1 (4 H, $CH_2C{=}C$, m), 5.35-5.55 (5.45, 5.35, 5.6) (3 H, $CH{=}CH_2$, m), 5.6-6.4 (4 H, CH=CH—CH=CH, m). Found, %: C 87.83; H 12.17. $C_{12}H_{20}$. Calculated, %: C 87.81; H 12.19.

(E,E)-Dodeca-8,10-dienol (VII). By a method similar to that for the synthesis of compound (III), 1.64 g (0.01 mole) of the triene (VI) yielded 1.06 g (58%) of the alcohol (VII) with bp 120-122°C (0.5 mm), mp 28-29°C; its IR and PMR spectra were identical with those given in the literature [12]. UV spectrum (λ_{max}): 229 nm (ε 22,800). Mass spectrum (m/z (I, %)): 182 M^+ (8.0), 180 ($M^+ - 2H$) (3.3), 164 ($M^+ - H_2O$) (0.35), 135 (2.5), 121 (3.0), 107 (3.5), 81 (100), 68 (75), 55 (50).

SUMMARY

A new stereospecific syntheiss of (E,E)-dodeca-8,10-dienol — the sex pheromone of the codling moth — has been developed on the basis of selective transformations of a readily accessible co-oligomer of butadiene and trimethylvinylsilane (deca-1,4,9-trien-1-ylsilane).

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