

INSECT PHEROMONES AND THEIR ANALOGS

LIX. A NEW METHOD FOR THE SYNTHESIS OF COMPONENTS

OF THE SEX PHEROMONES OF INSECTS OF THE GENUS *Malacosoma*

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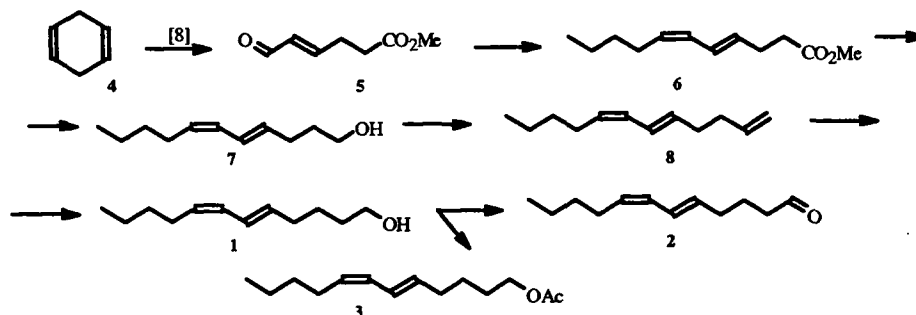
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A new method has been developed for the synthesis of the main components of the sex pheromones of insects of the Malacosoma genus that is based on the selective transformation of the product of the partial ozonolysis of cyclohexa-1,4-diene — methyl 6-oxohex-4E-enoate.

The isolation and identification of the sex pheromone of females of the lackey moth (*Malacosoma neustria*), a dangerous pest of fruit trees and forest species, showed that its main components are dodeca-5E,7Z-dien-1-ol (1) and the aldehyde corresponding to it (2) [1, 2]. Together with other components, the pheromone also contains the acetate (3) of alcohol (1). In biological trials, males reacted both to the aldehyde (2) and to a 1:1 mixture of it with the alcohol (1). The aldehyde (2) has also been identified as the sole component of the sex pheromone of a North American species of the *Malacosoma* genus — *M. disstria* [3].

In known studies on the synthesis of dodeca-5E,7Z-dien-1-ol (1), the Wittig olefination of α,β -unsaturated aldehydes of the E-configuration was used to construct the (E,Z)-dienic system [4—6]. In the present paper we describe a new route to the synthesis of the above-mentioned three components of the sex pheromone of the lackey moth, based on the ozonolytic cleavage of cyclohexa-1,4-diene (4), which is readily obtainable by the Birch hydrogenation of benzene [7].

We have previously reported [8] that on the partial ozonolysis of cyclohexa-1,4-diene with the subsequent treatment of the ozonolysis product with a mixture of Et_3N and Ac_2O the double bond remaining after ozonolysis shifts into conjugation with the aldehyde group to form methyl 6-oxohex-4E-enoate (5), which is a convenient synthon for the construction of the (E,Z)-dienic system.



Olefination of the aldehydoester (5) with $\text{Ph}_3\text{P}=\text{CH}(\text{CH}_2)_3\text{CH}_3$ took place with the formation of methylundeca-4E,6Z-dienoate (6). To lengthen the carbon skeleton by one carbon atom, the ester (6) was reduced to undeca-4E,6Z-dien-1-ol (7) with subsequent oxidation of the hydroxy function by $\text{Py}\cdot\text{CrO}_3\cdot\text{HCl}$ to the corresponding aldehyde and the use of the latter in a Wittig reaction with $\text{Ph}_3\text{P}=\text{CH}_2$. The dodeca-1,5E,7Z-triene obtained (8) reacted selectively with 9-BBN at the terminal double bond,

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and, after oxidation of the organoboron intermediate, gave one of the final products — the alcohol (1). Oxidation of the latter with $\text{Py}\cdot\text{CrO}_3\cdot\text{HCl}$ gave the aldehyde (2), and acetylation with Ac_2O in Py the acetate (3).

According to capillary GLC, the content of the main (5*E*,7*Z*)-stereoisomer in the final product was 95%.

EXPERIMENTAL

The IR spectra of the substances were taken on a UR-20 instrument in a thin layer or in Nujol. PMR spectra were obtained on a Bruker AM-300 spectrometer (working frequency 300 MHz) in CDCl_3 solution relative to TMS. ^{13}C NMR spectra were taken on a Bruker AM-300 spectrometer (working frequency 75 MHz) with CDCl_3 as solvent and TMS as internal standard. GLC analysis was conducted on a Chrom-5 chromatograph with glass columns (3×1200 mm), the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.16–0.20 mm), working temperature 50–300°C (rate of rise 12 deg/min), carrier gas helium. The analyses of all the compounds corresponded to the calculated values.

Methyl Undeca-4*E*,6*Z*-dienoate (6). In small portions, 5.7 g (33.2 mmole) of HMDS-Na was added to a suspension of 13.7 g (33.2 mmole) of $\text{Ph}_3\text{P}^+(\text{CH}_2)_4\text{CH}_3\text{Br}^-$ in 130 ml of absolute THF (argon) at -20°C and the mixture was stirred at -20°C for 0.5 h and was then cooled to -78°C and 3.6 g (25.3 mmole) of the aldehydoester (5) (obtained as described in [8]) was added.

The reaction mixture was stirred at -78°C for 1 h and at 20°C for 12 h, and it was then diluted with 300 ml of hexane, filtered through a small layer of silica gel, and evaporated, and the residue was chromatographed (SiO_2 , hexane—ether (9:1)) to give 3.8 g (76.3%) of the dienic ester (6)

IR spectrum (ν , cm^{-1}): 950, 990, 1620, 1650 ($\text{HC}=\text{CHCH}=\text{CH}$), 1160 (COOCH_3), 1745 ($\text{C}=\text{O}$).

PMR spectrum (300 MHz, CDCl_3 , ppm, J, Hz): 0.88 (3H, t, CH_3 , $J=7$), 1.20-1.40 (4H, m, H-9, H-10), 2.10 (2H, m, H-8), 2.40 (4H, m, H-2, H-3), 3.63 (3H, s, OCH_3), 5.33 (1H, m, $J=7$), 5.63 (1H, m, H-4), 5.90 (1H, m, H-6), 6.33 (1H, m, H-5).

^{13}C NMR spectrum (75 MHz, CDCl_3): 13.95 (q, C-11), 21.95 (t, C-10), 26.80 (t, C-9), 30.21 (t, C-8), 32.03 (t, C-3), 33.76 (t, C-2), 51.40 (q, OCH_3), 127.45 (d, C-7), 128.04 (d, C-6), 131.23 (d, C-4), 132.12 (d, C-5), 173.10 (s, $\text{C}=\text{O}$).

Found %: C 74.28; H 10.5; $\text{C}_{12}\text{H}_{10}\text{O}_2$. Calc. %: C 73.43; H 10.27.

Undeca-4*E*,6*Z*-dien-1-ol (7). At -10°C , 1 g (26.3 mmole) of LiAlH_4 was added in portions to a stirred solution of 3.8 g (19.4 mmole) of the ester (6) in 100 ml of absolute ether (argon) and the mixture was stirred for 1 h at -10°C and was kept at 20°C for 2 h, after which 8 ml of H_2O was added dropwise. The resulting precipitate was filtered off, the filtrate was evaporated, and the residue was passed through a thin layer of silica gel. This gave 3.1 g (96%) of the alcohol (7)

IR spectrum (ν , cm^{-1}): 940, 975, 1615, 1650 ($\text{C}=\text{C}$), 3360 ($\text{C}-\text{OH}$).

PMR spectrum (300 MHz, CDCl_3 , ppm, J, Hz): 0.87 (3H, t, CH_3 , $J=7$), 1.20-1.40 (4H, m, H-9, H-10), 1.58 (2H, m, H-2), 2.0-2.25 (4H, m, H-3, H-8), 3.71 (2H, t, OCH_2 , $J=6.5$), 5.34 (1H, m, $J=7$), 5.62 (1H, m, H-4), 5.90 (1H, m, H-6), 6.25 (1H, m, H-5).

Found %: C 78.92; H 12.3; $\text{C}_{11}\text{H}_{20}\text{O}$. Calc. %: C 78.51; H 9.51.

Dodeca-1,5*E*,7*Z*-triene (8). At 15°C , in a current of argon, 2.5 g (14.9 mmole) of the alcohol (5) in 5 ml of CH_2Cl_2 was added dropwise to a solution of 4.8 g (22.3 mmole) of $\text{Py}\cdot\text{CrO}_3\cdot\text{HCl}$ in 30 ml of absolute CH_2Cl_2 . The reaction mixture was stirred at 20°C for 3 h, diluted with 30 ml of CH_2Cl_2 and filtered through a thin layer of silica gel. The solvent was evaporated, and the residue was chromatographed (SiO_2 , hexane—ether (9:1)). This gave 2.1 g of an aldehyde, a solution of which in 8 ml of THF was added dropwise at -70°C to the ylide prepared from 5.8 g (16.2 mmole) of $\text{Ph}_3\text{P}^+\text{CH}_3\text{Br}^-$ and 2.8 g (16.3 mmole) of HMDS-Na in 50 ml of absolute THF at -20°C . The reaction mixture was stirred at -70°C for 1 h and at 20°C for 12 h, and 200 ml of hexane was added. The resulting precipitate was filtered off through a thin layer of silica gel, the filtrate was evaporated, and the residue was chromatographed (SiO_2 , hexane—ether (9:1)). This gave 1.5 g (61.5%) of the triene (8).

IR spectrum (ν , cm^{-1}): 925, 950, 980, 1620, 1650, 3090 ($\text{CH}=\text{CH}_2$, $\text{CH}=\text{CHCH}=\text{CH}$).

PMR spectrum (300 MHz, CDCl_3 , ppm): 0.87 (3H, t, CH_3 , $J=7$ Hz), 1.20-1.40 (4H, m, H-10, H-11), 2.00-2.37 (6H, m, H-3, H-4, H-9), 4.80-5.10 (2H, m, H-1), 5.30 (1H, m, H-8), 5.60 (1H, m, H-5), 5.79 (1H, m, H-2), 5.92 (1H, m, H-7), 6.30 (1H, m, H-6).

^{13}C NMR spectrum (75 MHz, CDCl_3): 13.29 (q, C-12), 22.10 (t, C-11), 26.15 (t, C-10), 30.30 (t, C-4), 31.69 (t, C-5), 34.86 (t, C-3), 112.70 (t, C-1), 126.77 (d, C-8), 128.30 (d, C-7), 131.22 (d, C-5), 134.76 (d, C-6), 139.47 (d, C-2).

Found %: C 87.50; H 11.96; C₁₂H₂₀. Calc. %: C 87.73; H 12.27.

Dodeca-5E,7Z-dien-1-ol (1). A solution of 1 g (6 mmole) of triene (8) in 4 ml of THF was added at 10°C in a current of argon to a suspension of 1 g (7.7 mmole) of 9-BBN in 10 ml of absolute THF. The mixture was stirred for 2 h, cooled to 0°C, and treated dropwise with 4.5 ml of 3 N NaOH solution and then with 5 ml of 30% H₂O₂ solution. The reaction mixture was stirred at 25°C for 2 h, diluted with 50 ml of ether, washed with 0.1 N Na₂S₂O₃ and a saturated solution of NaCl, and dried with MgSO₄. After evaporation, the residue was chromatographed (SiO₂, hexane—ether (4:1)). This gave 0.77 g (60%) of the dienol (1), the IR and PMR spectra of which were identical with those given in [6].

Dodeca-5E,7Z-dienal (2). The oxidation of 0.37 g (2.1 mmole) of the alcohol (1) with 0.65 g (3 mmole) of Py·CrO₃·HCl in 10 ml of CH₂Cl₂ under the conditions described for compound (7) led to 0.31 g (84.2%) of the dienal (2). Its IR and PMR spectra were identical with those given in [6].

Dodeca-5E,7Z-dien-1-yl Acetate (3). To 0.37 g (2.1 mmole) of the alcohol (1) was added 2.5 ml of a mixture (2:3) of Ac₂O and Py, and the resulting reaction mixture was stirred at room temperature for 15 h, diluted with 30 ml of ether, and washed successively with 10% HCl and saturated solutions of NaHCO₃ and NaCl, dried with Na₂SO₄, and evaporated. The residue was chromatographed (SiO₂, hexane—ether (9:1)), with the isolation of 0.39 g (86.6%) of the acetate (3), the IR and PMR spectra of which were identical with those given in [6].

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