INSECT PHEROMONES AND THEIR ANALOGUES

XXXI. SYNTHESIS OF DEC-5Z-EN-1-YL ACETATE AND HENEICOS-6Z-EN-11-ONE FROM A FUNCTIONALLY DIFFERENTIATED PRODUCT OF THE OZONOLYSIS OF CYCLOPENTENE

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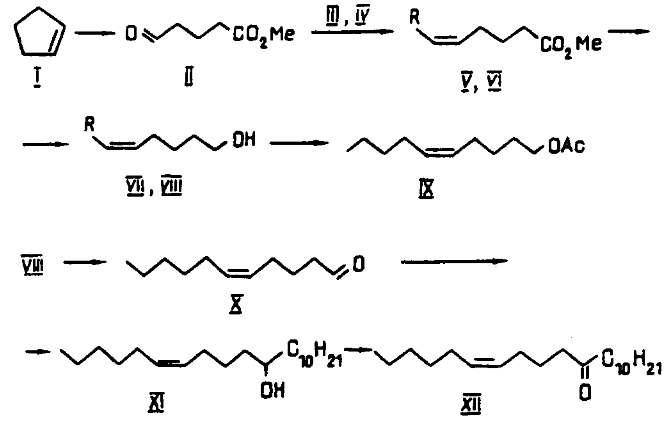
UDC 542.943+547.31+632.936

Dec-5Z-en-1-yl acetate and heneicos-6Z-en-11-one — pheromones of insects of the genera Agrotis and Orgyia, respectively — have been synthesized from a product of the functionally differentiated ozonolysis of cyclopentene.

The functionally differentiated ozonolysis of cyclic alkenes has opened up a convenient route to the synthesis of pheromones of insects of the order Lepidoptera [1]. From a product of the ozonolysis of cyclopentene (I) (methyl 5-oxopentanoate) we have synthesized dec-5Z-en-1-ol (VII) and undec-5Z-en-1-ol (VIII). The acetate of the former is a component of pheromones of insects of the genus Agrotis [2]. From compound (VIII) we have synthesized heneicos-6Z-en-11-one (XII) — the sex pheromone of tussock moths of the genus Orgyia, which are pests of fir forests [2].



$RCH{=}PPh_3$, where R = $n\text{-}C_4H_9$ (III, V, VIII); $n\text{-}C_5H_{11}$ (IV, VI, VIII)

The conversion of the aldehydo ester (II) into the desired compounds (VII) and (VIII) was achieved by the Wittig reaction with the appropriate phosphoranes (III) and (IV), followed by the reduction of the esters obtained (V) and (VI) with the aid of diisobutylaluminum hydride. According to the ^{13}C NMR results for the ester (VI) and the GLC analysis of (V) and (VI),* the olefination of the aldehydo ester (II) took place exclusively stereospecifically with the formation of a (Z)-double bond, which agrees with results that we have obtained previously for other aldehydo esters [1]. The acetylation of the alcohol (VII) gave the desired acetate (IX).

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*The stereochemistry of the individual compounds (V) and (VI) was shown by the single peak in each of their chromatograms. Their (Z)-configurations were unambiguously confirmed by the signals of the allyl C^4 and C^7 carbon atoms in the regions of δ 27.22 and 26.57 ppm.

Institute of Chemistry, Bashkir Scientific Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 568-571, July-August, 1991. Original article submitted June 12, 1990.

0009-3130/91/2704-0497$12.50

Oxidation of the alcohol (VIII) followed by condensation of the aldehyde (X) with n-decylmagnesium bromide according to [3] gave heneicos-6Z-en-11-ol(XI), oxidation of which led to the pheromone (XII).

The yields of the pheromones (IX) and (XII) calculated on the initial cyclopentene were 33 and 31%, 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 (100 MHz) spectrometer, with $CDCl_3$ as solvent and TMS as internal standard. The ^{13}C NMR spectrum for compound (VI) was taken on a Bruker-300 (300 MHz) instrument in $CDCl_3$. Mass spectra were run on a MKh-1320 instrument with the aid of a direct-introduction system at a temperature of the ionization chamber of 100-150°C and ionizing voltage of 70 eV.

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), (IX), (X), and (XII) or PEG-20 m (15%) (for compounds (VII) and (VIII)] or with a 3 × 2400 mm stainless steel column containing the stationary phase FFAP (5%) [for compounds (V) and (VI)] on the support Chromaton N-AW-DMCS; flame ionization detector, carrier gas helium, working temperature 50-250°C.

The GLC analysis of compounds (V) and (VI) was also conducted on a Shimadzu instrument with a 0.2 × 25,000 mm glass capillary column and the stationary phase PEG-20 m, at a working temperature 100°C, with helium as the carrier gas. R_f values are given for a fixed layer of SiO_2 of the Silufol type, the revealing agent being iodine.

Methyl 5-Oxopentanoate (II). A mixture of ozone and oxygen was bubbled at the rate of 30 liters/h (the productivity of the ozonizer being 55 mmoles of O_3/h) through a solution of 5.0 g (73.5 mmoles) of cyclopentene (I) in 88 ml of a 5:1 mixture of methylene chloride and methanol containing a suspension of 6.17 g (73.5 mmoles) of $NaHCO_3$ at −70°C until the ozone broke through (1.34 h; monitoring by starch-iodide indicator paper). The reaction mixture was purged with argon and was treated at −20°C with 3.7 ml of acetic anhydride and 5.5 ml of triethylamine. The resulting mixture was stirred for 5 h and was left at 8°C for 15 h, and it was then evaporated and the residue was diluted with 200 ml of diethyl ether. The ethereal solution was washed successively with saturated solution of NH_4Cl, $NaHCO_3$, and NaCl, and it was dried over $MgSO_4$ and evaporated, and the residue was distilled in vacuum. This gave 5.76 g (60%) of the aldehydo ester (II), bp 97-98°C (26 mm), n_D^{26} 1.4278. IR spectrum (ν, cm^{-1}): 852, 880, 1008, 1052, 1080, 1168, 1188, 1200, 1236, 1248, 1312, 1328, 1368, 1436, 1720, 1732, 1740, 2728, 2776, 2848, 2864, 2952. PMR spectrum (δ, ppm): 1.72-2.0 (2H, m, H-3), 2.13-2.58 (4H, m, H-2 and H-4), 3.6 (3H, s, OCH_3), 9.67 (1H, s, H-5).

Methyl Dec-5Z-enoate (V). A suspension of 6.64 g (16.15 mmoles) of n-pentyltriphenylphosphonium bromide (obtained according to [4]) in 60 ml of dry THF was treated at −30°C with 1.77 g (16.15 mmoles) of tert-BuOK, the mixture was stirred for 20 min (Ar) and was then cooled to −78°C, and to the ylide so obtained was added, dropwise, 1.4 g (10.78 mmoles) of the aldehydo ester (II) in 6 ml of dry THF. The reaction mixture was stirred at −78°C for 2 h and was allowed to warm up to room temperature over 1 h and was left for 15 h. The usual working up gave 1.2 g (60%) of the alkenoate (V), bp 59-61°C (1 mm), n_D^{22} 1.4191, R_f 0.55 [hexane–ether (9:1)].

IR spectrum (ν, cm^{-1}): 750, 880, 930, 1040, 1070, 1130, 1170, 1230, 1240, 1320, 1370, 1445, 1465, 1660, 1745, 2870, 2980, 3020. PMR spectrum (δ, ppm): 0.89 (3H, t, J = 6.3 Hz, H-10), 1.16-1.42 (4H, m, H-8, H-9), 1.68 (2H, m, H-3), 1.92-2.15 (4H, m, H-4, H-7), 2.32 (2H, t, J = 7.4 Hz, H-2), 3.67 (3H, s, OCH_3), 5.16-5.27 (2H, m, H-5, H-6). Mass spectrum, m/z (%): 184 (M^+, 8.33), 153 ($M - OCH_3^+$, 9.67), 152 ($M - CH_3OH^+$, 22.67), 135 (7.67), 124 ($M - HCO_2CH_3^+$, 5.33), 123 (10.67), 111 (9.67), 110 ($M - CH_3CO_2CH_3^+$, 58.33), 96 (24.67), 95 (14.0), 87 (14.67), 84 (14.67), 81 (43.33), 74 (100), 69 (30.33), 68 (23.67), 67 (27), 59 (10.67), 55 (58.33), 54 (27), 43 (32.67), 41 (43.33).

Methyl Undec-5Z-enoate (VI). Under the conditions described for compound (V), 1.4 g (10.77 mmoles) of the aldehydo ester (II), 6.0 g (14 mmoles) of n-hexyltriphenylphosphonium tribromide (obtained according to [4]), and 1.53 g (14 mmoles) of tert-BuOK yielded 1.28 g (60%) of the ester (VI), bp 62°C (1 mm), $n_D^{21.5}$ 1.4412, R_f 0.52 [hexane–ether (9:1)]. IR spectrum (ν, cm^{-1}): 750, 790, 880, 1040, 1075, 1130, 1165, 1250, 1330, 1375, 1445, 1465, 1660, 1745, 2830, 2930, 2980, 3020. PMR spectrum (δ, ppm): 0.88 (3H, t, J = 6.4 Hz, H-11), 1.23-1.48 (6H, m, H-8, H-9, H-10), 1.62-1.85 (2H, m, H-3), 1.90-2.20 (4H, m, H-4, H-7), 2.32 (2H, t, J = 7.4 Hz, H-2), 3.67 (3H, s, OCH_3), 5.22-5.55 (2H, m, H-5, H-6). ^{13}C NMR spectrum (δ, ppm): 51.43 (OCH_3), 174.14 (C-1), 33.50 (C-2), 24.96 (C-3), 27.22 (C-4), 128.36 and 131.22 (C-5 and C-6), 26.57 (C-7), 29.40 (C-8), 31.54 (C-9), 22.59 (C-10), 14.07 (C-11).

Mass spectrum, m/z (%): 198 (M^+, 12.57), 167 ($M - OCH_3{}^+$, 10.0), 166 ($M - CH_3OH^+$, 20.86), 149 (11.14), 138 ($M - CH_3CO_2H^+$, 4.7), 137 (7.25), 125 (9.1), 124 (54.7), 123 (14.4), 110 (12.35), 109 (10.3), 98 (10.76), 97 (18.23), 96 (52.94), 95 (22.06), 87 (25.0), 84 (50), 83 (28.8), 82 (54.4), 81 (52.9), 78 (27.94), 74 (100), 69 (48.58), 68 (32.35), 67 (47.06), 59 (23.53), 55 (70.59), 54 (49.41), 43 (42.65), 41 (67.65), 39 (19.41), 28 (23.53), 26 (16.76), 15 (11.18).

Dec-5Z-en-1-ol (VII). With stirring (−10°C, Ar) a mixture of 3.5 ml of a 73% toluene solution of $(iso\text{-}C_4H_9)_2AlH$ and 3 ml of absolute diethyl ether was slowly added dropwise to a solution of 1.1 g (5.9 mmoles) of the ester (V) in 22 ml of absolute diethyl ether, and the mixture was stirred at 0°C for 2 h and was then gradually heated to room temperature and was left for 15 h. After this, at 0°C, with stirring, 3.7 ml of water was added, the mixture was heated to room temperature and was stirred for 1 h, and the precipitate was filtered off and was carefully washed with diethyl ether—benzene (8:1). The filtrate was dried with $MgSO_4$ and was evaporated (in vacuum) to give 0.88 g (95%) of the alcohol (VII). Its IR and PMR spectra were identical with those given in [5].

Undec-5Z-en-1-ol (VIII). Under the conditions described for compound (VII), 1.2 g (6.1 mmoles) of the ester (VI) and 3.7 ml of a 73% toluene solution of $(iso\text{-}C_4H_9)_2AlH$ yielded 0.98 g (95%) of the alcohol (VIII). Its IR and PMR spectra were identical with those given in [3].

Dec-5Z-en-1-yl Acetate (IX). A solution of 0.8 g (5.1 mmoles) of the alcohol (VII) in 12.75 ml of acetic anhydride—pyridine (2:3) was kept at room temperature for 24 h, and, after the addition of 250 ml of diethyl ether, it was washed successfully with 5% HCl and saturated solutions of $NaHCO_3$ and NaCl, and it was dried with $MgSO_4$ and evaporated. This gave 0.98 g (97%) of the acetate (IX). Its IR and PMR spectra were identical with those given in [5].

Heneicos-6Z-en-11-one (XII). Via the intermediate compounds (X) and (XI), under the conditions given in [3], 0.98 g (5.7 mmoles) of the alcohol (VIII) gave 1.6 g of the ketone (XII) (yield in three stages 90%). Its IR and PMR spectra were identical with those given in [3].

LITERATURE CITED

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