INSECT PHEROMONES AND THEIR ANALOGS

III. SYNTHESIS OF THE SEX ATTRACTANTS OF SOME LEPIDOPTERA

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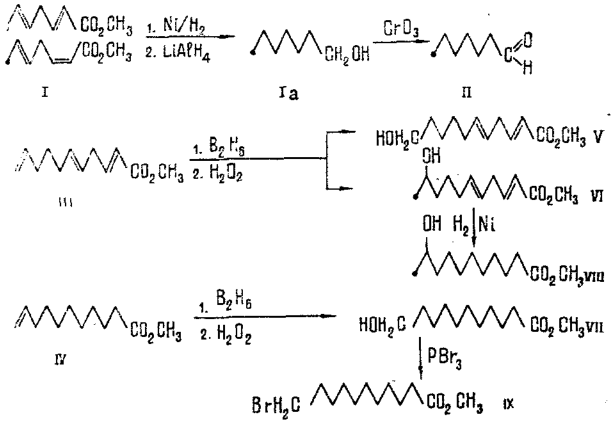
A new route to the synthesis of a number of attractants of Lepidoptera (Argyrotaenia velutinana, Mamestra configurata, and Lycorea ceres ceres) have been developed. These substances are acetates of enols with the cis configuration: tetradec-11-en-1-ol, hexadec-11-en-1-ol, and octadec-11-en-1-ol, respectively. The constants of the substances obtained agree completely with those given in the literature. The method is based on the coupling of the C_3, C_5, and C_7 aldehydes with methyl 11-bromoundecanoate (I) by the Wittig reaction. To obtain compound (I) from methyl undeca-2E,5E,10-trienoate or methyl undeca-10-enoate we used hydroboration according to Brown followed by hydrogenation and bromination of the alcohol obtained. The advantage of this method is the use as starting materials of esters of unsaturated acids readily obtained by the homogeneous catalytic co-oligomerization of 1,3-dienes with acrylates.

A promising direction in the synthesis of the sex attractants of insects is the use of esters of unsaturated acids obtained by the homogeneous catalytic co-oligomerization of 1,3-dienes with acrylates [1-4]. The present paper describes a new route for the synthesis of a number of attractants of lepidoptera (Argyrotaenia velutinana, Mamestra configurata, and Lycorea ceres ceres) [5-9] based on the coupling of C_3, C_5, and C_7 aldehydes with methyl 11-bromoundecanoate by the Wittig reaction. As the C_3-C_7 fragments we used propionaldehyde, n-valeraldehyde, and n-heptanal. The latter was synthesized from a mixture of hepta-2Z(E),5E-dienoic acids (I) [4] by its successive hydrogenation on Raney nickel, reduction with $LiAlH_4$ in ether, and oxidation to heptanal (II) by Corey's method [10]. To obtain methyl 11-bromoundecanoate we used esters of undeca-2E,5E,10-trienoic acid (III) [3] and of undeca-10-enoic acid (IV) [7].



Scheme 1

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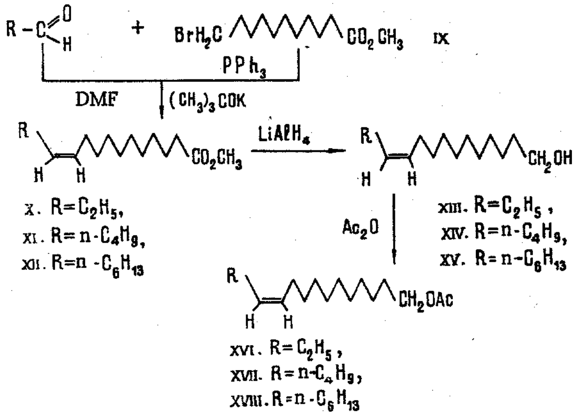

Scheme 2

Thus, the hydroboration of (III) with B_2H_6 in THF followed by treatment of the reaction products with 30% H_2O_2 in an alkaline medium [11] gave a mixture of the unsaturated alcohols (V) and (VI) in a ratio of 9 : 1 with a total yield of 50% calculated on the initial ester. The hydrogenation of (V) and (VI) on Raney nickel in ethyl acetate led to a mixture of methyl 11- and 10-hydroxyundecanoic acids (VII and VIII) in quantitative yield.

The structures of (VII) and (VIII) were confirmed by spectral methods, and also by comparison with authentic samples [3, 9, 12].

In contrast to (II), the hydroboration of (IV) took place with an exceptional selectivity and, after oxidation with H_2O_2, only (VII) was formed, in an overall yield of 90%. The treatment of the alcohol (VII) with PBr_3 in benzene gave the 11-bromoundecanoate (IX) with a yield of ~85% [8] (Scheme 1).

The reactions of the triphenylphosphonium salt (IX) with the above-mentioned aldehydes in dimethylformamide under the action of tert-BuOK [2] gave the methyl esters of tetradec-11Z-enoic (X) [12], hexadec-11Z-enoic (XI) [13], and octadec-11Z-enoic (XII) [9] acids with yields of 65%.

It must be mentioned that in all the experiments, in addition to (X-XII), the corresponding trans isomers were formed, but their amounts in the mixture of products did not exceed 5-6%. Unfortunately, because of their close boiling points the separation of the cis and trans isomers is a difficult problem.

The reduction of (X-XII) with $LiAlH_4$ in ether led to the alcohols (XIII-XV) [7-9], the acetylation of which with $(CH_3CO)_2O$ in pyridine gave quantitative yields of the extractants of Argyrotaenia velutinana (XVI), Mamestra configurata (XVII), and Lycorea ceres ceres (XVIII) (Scheme 2).

Thus, we have developed a new method for obtaining a series of attractants of Lepidoptera the synthesis of which is based on the use of readily available esters of unsaturated acids.

EXPERIMENTAL

The unsaturated esters (I) and (II) that were used had a purity of not less than 98%. Analysis of the compounds obtained was carried out on a Khrom-41 chromatograph with a 3-m column containing 15% of SE-30. ^1H NMR spectra were recorded on a Tesla 480 BS instrument in $CDCl_3$ solution (internal standard HMDS). IR spectra were recorded on a UR-20 instrument (film) and mass spectra on a MKh-1306 instrument with an energy of the ionizing electrons of 70 eV at a chamber temperature of 200°C.

General Procedure for the Hydroboration of the Esters (III) and (IV) with B_2H_6. At 20 °C, B_2H_6 obtained by the method of Brown and Zweifel [11] from 10 g of $BF_3 \cdot O(C_2H_5)_2$ and 1.6 g of $NaBH_4$ in 40 ml of diglyme was bubbled through a solution of 20 g of (III) or (IV) in 250 ml of absolute diglyme for 5 h. Then 35 ml of 3 N NaOH solution and 35 ml of 30% H_2O_2 were added successively to the reaction mixture. The resulting mixture was stirred at room temperature for 3 h and was then left overnight. Then it was extracted with ether (3 × 150 ml). The combined ethereal extracts were carefully washed with water and dried over $MgSO_4$ and, after elimination of the solvent, the residue was distilled. This gave 50 g of a mixture of alcohols consisting, according to GLC, of 85% of (V) and 15% of (VI). The alcohols (V) and (VI) isolated by redistillation in vacuum had the following constants:

Methyl 11-Hydroxyundeca-2E,5E-dienoate (V). bp 158-160°C (0.5 mm), n_D^{20} 1.4822. IR spectrum ν, cm^{-1}): 975, 3030 (trans-CH =CH–), 1245, 1735 ($-CO_2CH_3$) and 3400 (OH). PMR spectrum (δ, ppm): 1.50 (4H, $-CH_2-$), 2.0 (4H, $-CH_2-C=$), 2.88 (2H, $=C-CH_2-C=$), 3.45 (2H, $-CH_2O-$), 3.58 (3H, CH_3-O-), 5.56 (4H, $-CH=CH-$); M^+ 212.

Methyl 10-hydroxyundeca-2E,5E-dienoate (VI). bp 145-147°C (0.5 mm), n^{20}_D 1.4787. IR spectrum (ν, cm^{-1}): 976, 3030 (trans-CH = CH–), 1245, 1735 (CO_2CH_3) and 3400 (OH). PMR spectrum (δ, ppm): 0.85 (3H, CH_3-C), 1.51 (4H, $-CH_2-$), 1.95 (2H, $-CH_2-C=$), 2.87 (2H, $=C-CH_2-C=$), 3.55 (3H, CH_3O-), 4.10 (1H, CH–O), 5.40 (4H, –CH = CH –); M^+ 212.

The hydrogenation of (V) and (VI) over Raney nickel in ethyl acetate (H_2, 100 atm, 80°C, 4 h) led to the hydroxy esters (VII) and (VIII), in quantitative yield.

Methyl 11-hydroxyundecanoate (VII). bp 140-143°C (0.5 mm), n_D^{20} 1.4552. IR spectrum (ν, cm^{-1}): 1245, 1740 (CO_2CH_3) and 3400 (OH). Found %: C 67.47, H 11.20, $C_{12}H_{24}O_3$. Calculated %: C 66.97, H 11.04. M^+ 216.

Under conditions similar to those described for the preparation of the ester (VII) by the hydroboration of (III), 75 g of (IV) yielded 65.5 g of (VII), the constants of which coincided completely with those of the above preparation of this substance.

Methyl 10-Hydroxyundecanoate (VIII). bp 125-127°C (0.5 mm), n_D^{20} 1.4522. IR spectrum (ν, cm^{-1}): 1245, 1737 (CO_2CH_3) and 3400 (OH). Found %: C 67.25, H 10.95, $C_{12}H_{24}O_3$. Calculated %: C 66.97, H 11.04. M^+ 216.

Methyl 11-Bromoundecanoate (IX). At 5-10°C, 10 ml of PBr_3 in 40 ml of benzene was added to a solution of 50 g of (VII) in 200 ml of dry benzene. Then the mixture was stirred at room temperature for 5 h, 40 ml of H_2O was added, and the organic layer was separated off, washed repeatedly with water, and dried over $MgSO_4$. After elimination of the solvent, the residue was distilled in vacuum giving 55 g (85%) of (IX). bp 120-123°C (0.5 mm), n_D^{20} 1.4770. IR spectrum (ν, cm^{-1}): 1245, 1735 (CO_2CH_3). PMR spectrum (δ, ppm): 1.26 (16H, $-CH_2-$) 2.21 (2H, $-CH_2-\underset{\underset{O}{\|}}{C}-$), 3.32 (2H, $-CH_2Br$), 3.55 (3H, CH_3O-), M^+ 279.

Preparation of the Unsaturated Esters (XII-XIV). A. Synthesis of Triphenylphosphonium Derivative of (IX). A solution of 12.8 g of (IX) and 12 g of PBr_3 in 50 ml of acetonitrile was boiled for 8 h, and then the solvent was evaporated off and the residue was washed repeatedly with ether and was dried in vacuum. This gave 22 g of a syrupy oil. Found %: C 66.91, H 7.08, P 5.41, Br 14.52, $C_{30}H_{38}PO_2Br$. Calculated %: C 66.49, H 7.02, P 5.73, Br 14.80.

B. At 0 °C in a current of argon, 5.2 g of potassium tert-butanolate (obtained from 1.8 g of potassium and 50 ml of tert-butanol) was added over one hour to a solution of 22 g of the phosphonium derivative of (IX) in 50 ml of DMF, and the mixture was stirred at 20°C for 3 h. Then it was cooled to 0 °C, 6 g of heptanal (II) in 30 ml of DMFA was added and stirring was continued for 5 h. After the mixture had been cooled (0.5°C), 30 ml of H_2O was added and it was extracted repeatedly with benzene. The combined extracts were dried over $MgSO_4$ and filtered through 100 g of Al_2O_3 (activity grade III). The solvent was driven off and the residue was distilled in vacuum. This gave 8.8 g (64.5%) of (XII). bp 145-147°C (0.5 mm), n_D^{20} 1.4554. IR spectrum (ν, cm^{-1}): 720, 3030 (cis –CH = CH–), 1245, 1735 (CO_2CH_3). PMR spectrum (δ, ppm): 0.87 (3H, $CH_3-\overset{|}{C}<$), 1.26 22H, $-CH_2-$), 1.98 (4H, $=C-CH_2-$), 2.13 (2H, $-CH_2-\underset{\underset{O}{\|}}{C}-$), 3.56 (3H, CH_3O-), 5.25 (2H, –CH = CH–), M^+ 296.

The reaction of propionaldehyde and valeraldehyde with an equimolar amount of the triphenylphosphonium derivative of (IX) under the conditions described above gave the methyl esters (X) and (XI) with yields of 65% and 64.6%, respectively.

Methyl Tetradec-11Z-enoate (X). bp 110-112°C (0.5 mm), n_D^{20} 1.4495. IR spectrum (ν, cm^{-1}): 720, 3030 (cis –CH = CH–), 1246, 1735 (CO_2CH_3). PMR spectrum (δ, ppm): 0.87 (3H, $CH_3-\overset{|}{C}<$), 1.25 (14H, $-CH_2-$), 1.98 (4H, $=C-CH_2-$), 2.14 (2H, $-CH_2-\underset{\underset{O}{\|}}{C}-$), 3.55 (3H, CH_3-O-), 5.25 (2H, – CH = CH –), M^+ 240.

Methyl Hexadec-11-enoate (XI). bp 121-123°C (0.5 mm), n_D^{20} 1.4515. IR spectrum, (ν, cm^{-1}): 720, 3030 (cis–CH = CH–), 1245, 1735 (CO_2CH_3). PMR spectrum (δ, ppm): 0.86 (3H, $CH_3-\underset{|}{C}<$), 1.25 (18H, $-CH_2-$), 1.97 (4H, $=C-CH_2-$), 2.15 (2H, $-CH_2-\underset{\underset{O}{\|}}{C}-$), 3.55 (3H, CH_3-O), 5.25 (2H, –CH = CH–), M^+ 268.

General Procedure for Reducing the Esters (X-XII) with $LiAlH_4$. At room temperature, 10 g of the appropriate ester (X), (XI), or (XII) was added to a suspension of 3.5 g of $LiAlH_4$ in 50 ml of absolute diethyl ether, and then the mixture was boiled for 3 h. After this, it was cooled to 0 °C and was treated with 20 ml of H_2O, and the resulting precipitate was washed repeatedly with diethyl ether and the combined extracts were dried over $MgSO_4$. The solvent was driven off, and the residue was distilled in vacuum. The unsaturated alcohols (XIII-XV) obtained by this method had the following constants:

Tetradec-11Z-en-1-ol (XIII). bp 115-118°C (0.5 mm), n_D^{20} 1.4577. IR spectrum (ν, cm^{-1}): 720, 3030 (cis $-CH=CH-$), 3400 (OH). PMR spectrum (δ, ppm): 0.87 (3H, $CH_3-\overset{|}{C}<$), 1.25 (16H, $-CH_2-$). 1.98 (4H, $-CH_2-C=$), 3.58 (3H, $-CH_2-O-$), 4.0 (1H, $-OH$), 5.25 (2H, $-CH=CH-$), M^+ 212.

Hexadec-11Z-en-1-ol (XIV). bp 128-129°C (0.5 mm), n_D^{20} 1.4593. IR spectrum (ν, cm^{-1}): 720 , 3030 (cis $-CH=CH-$), 3600 (OH). PMR spectrum (δ, ppm): 0.87 (3H, $CH_3-\overset{|}{C}<$), 1.25 (24H, $-CH_2-$), 1.98 (4H, $=C-CH_2-$), 3.59 (2H, $-CH_2-O-$), 4.0 (1H, OH), 5.25 (2H, $-CH=CH-$), M^+ 240.

Octadec-11Z-en-1-ol (XV). bp 138-140°C (0 .5 mm), n_D^{20} 1.4635. IR spectrum (ν, cm^{-1}): 720, 3030 (cis $-CH=CH-$), 3600 (OH). PMR spectrum (δ, ppm): 0.87 (3H, $CH_3-\overset{|}{C}<$), 1.25 (24H, $-CH_2-$), 1.98 (4 H, $-CH=CH-$), 3.59 (2H, $-CH_2-O-$), 4.0 (1H, OH), 5.25 (2H, $-CH=CH-$), M^+ 268.

The acetylation of (XIII-XV) with an excess of acetic anhydride in pyridine at room temperature for 10 h led, after the usual working up, to the insect pheromones (XVI-XVIII) in quantitative yield, the constants of the products coinciding with those given in the literature [7, 9, 13].

Heptanal (II). At 0-5°C, 8 g of (Ia) in 30 ml of CH_2Cl_2 was added over 1 h to a suspension of 20 g of the Corey reagent [10] in 30 ml of freshly distilled CH_2Cl_2. The reaction mixture was stirred at room temperature for another 1 h and was then diluted with 100 ml of dry diethyl ether. The resulting precipitate was filtered off and washed with ether, and the combined ethereal extracts were washed with water and dried over $MgSO_4$. Elimination of the solvent and distillation of the residue gave 7.5 g of compound (II).

SUMMARY

A new approach is proposed to the synthesis of a number of attractants of Lepidoptera using as the starting compounds readily accessible unsaturated esters obtained by the co-oligomerization of 1,3-dienes with methyl acrylate.

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