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SYNTHESIS OF DODEC-5E-EN-1-OL — THE PHEROMONE OF TRICIMBA CINCTA — AND TETRADEC-5E-1-YL ACETATE — AN IMITATOR OF THE PHEROMONE OF RHYNCHOPACHA SP.

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On the basis of a modified Knoevenagel reaction starting from octanol and decanal, the stereodirected synthesis has been effected of dodec-5E-en-ol (the pheromone of the grass fly <u>Tricimba cincta</u> - and tetradec-5E-en-yl acetate) an imitator of the pheromone of the moth <u>Rhynchopacha sp.</u>

The attractant activity of dodec-5E-en-1-ol (I) for females of the grass fly <u>Tricimba</u> <u>cincta</u> (<u>Diptera</u>, <u>Chloropidae</u>) and of tetradec-5-en-1-yl acetate (II) for males of the moth <u>Rhynchopacha sp.</u> (<u>Lepidoptera</u>, <u>Gelechiidae</u>) has been established. The synthesis of these compounds based on the formation of an E-double bond on the opening of the cyclopropane rings in the corresponding alkyl cyclopropyl carbinols has been described [1].

Continuing investigations of the synthesis of alk-E-enols and their acetates on the basis of a modified Knevenagel reaction [2, 3], we propose a new approach to the synthesis of the attractants (I) and (II) (see scheme on following page).

The condensation of octanal (III) and decanal (IV) with malonic acid in boiling p-xylene in the presence of catalytic amounts of piperidine yielded dec-3-enoic (V) and dodec-3-enoic (VI) acids with yields of 68 and 70%, respectively. These acids were converted by the action of lithium tetrahydroaluminate in absolute ether into dec-3-en-1-ol (VII) and dodec-3-en-1ol (VIII) with yields of 65 and 60%, respectively. The bromination of the latter with PBr₃ in ether in the presence of traces of pyridine gave 1-bromodec-3E-ene (IX) and 1-bromododec-3E-ene (X) with yields of 67 and 60%, respectively. The condensation of the bromides (IX) and (X) with malonic ester in n-butanol in the presence of sodium butanolate, as described in [4], led, after alkaline hydrolysis, to a mixture of dec-3E-enylmalonic acid (XII) and its monobutyl ester (XII) or a mixture of dodec-3E-en-1-ylmalonic acid (XIII) and its monobutyl ester (XIV).

Subsequent thermal decarboxylation in the presence of Ionol gave the corresponding mixtures of dodec-5E-enoic acid (XVI) and its n-butyl ester (XVI) and tetradec-5E-enoic acid (XVII) and its n-butyl ester (XVIII). The yield of the acid (XV) was 47.6%, calculated on the bromide (IX) and that of its n-butyl ester (XVI) 12.8%; the yield of the acid (XVII) calculated on the bromide (X) was 40.6%, and that of its ester 14.7%. Reduction of the mixtures (XV and XVI) and (XVII and XVIII) of the alk-E-enoic acids and their butyl esters with lithium tetrahydroaluminate gave dodec-5E-en-1-ol (I) and tetradec-5E-en-1-ol (XIX) with yields of 72 and 76.6%, respectively. Acetylation of the alcohol (XIX) gave the attractant (II) with a yield of 77.2%.

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$$\begin{array}{c} \operatorname{CH}_{3}(\operatorname{CH}_{2})_{n}\operatorname{CHO}\rightarrow\operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2}\operatorname{COOH}\rightarrow \\ \operatorname{III, IV} & \operatorname{V, VI} \\ \rightarrow \operatorname{CH}_{3}(\operatorname{CH}_{3})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2})_{2}\operatorname{OH}\rightarrow\operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{3})_{2}\operatorname{Br} \\ \operatorname{VII-VIII} & \operatorname{IX, X} \\ \rightarrow \operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2})_{2}\operatorname{CH} & \begin{array}{c} \operatorname{COOR} \\ \rightarrow \operatorname{COOR}' \\ \operatorname{COOR}' \\ \end{array} \\ \rightarrow \operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2})_{3}\operatorname{COOR}'' \rightarrow \\ \operatorname{XV-XVIII} \\ \rightarrow \operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2})_{4}\operatorname{OH}\rightarrow \\ \operatorname{I, XIX} \\ \rightarrow \operatorname{CH}_{3}(\operatorname{CH}_{2})_{n-1}\operatorname{CH}\stackrel{E}{=}\operatorname{CH}(\operatorname{CH}_{2})_{4}\operatorname{OAc} \\ \end{array} \\ \begin{array}{c} \operatorname{II} \\ n = 6 (\operatorname{I, III, V, VII, IX, XI, XII, XV, XVI); \\ n = 8 (\operatorname{II, IV, VI, VIII, X, XIII, XIV, XVII); \\ \operatorname{R}=\operatorname{R}'=\operatorname{H}(\operatorname{XI, XIII}); \quad \operatorname{R}''=\operatorname{H}(\operatorname{XV, XVII}); \\ \operatorname{R}=\operatorname{H}_{n}\operatorname{R}'=\operatorname{H}-\operatorname{C}_{4}\operatorname{H}_{9}(\operatorname{XII, XIV}); \quad \operatorname{R}''=\operatorname{H}-\operatorname{C}_{4}\operatorname{H}_{9}(\operatorname{XVI, XVIII}) \end{array}$$

EXPERIMENTAL

IR spectra were recorded on a Specord 71IR instrument in chloroform, and PMR spectra on a Varian XL-200 instrument with a working frequency of 200 MHz. The solvent used was carbon tetrachloride, and the standard was tetramethylsilane, the signal of which was taken as 0. The purity of the substances and the course of the reactions were monitored by thinlayer chromatography on Silufol UV-254 plates. The spots were revealed with iodine vapor.

<u>Dec-3E-enoic Acid (V).</u> A mixture of 78.05 g (0.75 mole) of malonic acid, 32.05 g (0.25 mole) of octanol, and 21.25 mg (0.00025 mole) of piperdine in 200 ml p-xylene was boiled until the separation of water in a Dean-Stark trap had ceased (4 h). The solution was washed twice with water and was dried with MgSO₄. After evaporation and distillation, 28.9 g (68%) of the E- acid was obtained, by 123-126°C/2 mm. IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 1720 (CO). PMR spectrum (δ , ppm): 0.85 (3H, t, CH₃), 1.03-1.42 (8H, m, CH₂), 1.98 (2H, m, C=CH₂), 2.96 (2H, d, CH₂-CO, J = 6.0 Hz), 5.35-5.60 (2H, m, CH=CH).

According to the literature [2]: bp 110-112/1 mm.

<u>Dodec-3E-enoic Acid (VI)</u>. This was obtained in a similar way from 15.6 g (0.15 mole) of malonic acid, 7.8 g (0.05 mole) of decanal (IV), and 4.25 mg (0.05 mmole) of piperidine with a yield of 7.0 g (70%). bp 155-158°C/3 mm. Its IR and PMR spectra were identical with those described in the literature [3].

<u>Dec-3E-en-1-ol (VII)</u>. To a suspension of 6.14 g (0.16 mole) of lithium tetrahydroaluminate in 400 ml of ether was added, dropwise, 22.9 g (0.135 mole) of dec-3E-enoic acid (V) in 30 ml of absolute ether at such a rate that the reaction mixture boiled uniformly. After the end of the addition of acid, the mixture was stirred with heating for another 3 h. The excess of lithium tetrahydroaluminate was decomposed by the careful addition of water, and the precipitate that deposited was filtered off and was washed with ether (50 ml). The ethereal solution was dried with MgSO₄, and the solvent was evaporated off, giving 13.7 g (65%) of the alk-E-enol.

IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 3420 (OH). PMR spectrum (δ , ppm): 0.85 (3H, t, CH₃), 0.96 (H, s, OH), 1.1-1.4 (8H, m, CH₂), 1.93 (2H, m, CH₂-C=C), 2.14 (2H, m, C=C-CH₂), 3.45 (2H, t, CH₂O, J = 6.5 Hz), 5.2-5.5 (2H, m, CH=CH, J = 15.1 Hz).

<u>Dodec-3E-en-1-ol (VIII)</u>. This was obtained in a similar way from 1.44 g (0.038 mole) of lithium tetrahydroaluminate and 6.3 g (0.032 μ mole) of dodec-3E-enoic acid (VI) with a yield of 3.5 g (60%). Its spectral characteristics corresponded to those given in the literature [3].

<u>1-Bromodec-3E-ene (IX).</u> In drops, 24.09 g (0.089) mole of PBr₃ was added with stirring and cooling (-5 to 0°C) to a mixture of 13.7 g (0.089 mole) of dec-3E-en-1-ol (VII) and four drops of pyridine in 40 ml of absolute ether. On the following day the mixture was boiled for 2 h and, after cooling, was poured onto ice (50 g), and the ethereal layer was separated off, washed with 5% NaHCO₃ solution and with water, and was dried with MgSO₄. After elimination of the solvent and fractionation, 6.44 g (67%) of the bromide (IX) was obtained with bp 76-78°C/2 mm. PMR spectrum (δ , ppm): 0.84 (3H, t, CH₃), 1.1-1.4 (8H, m, CH₂), 1.95 (2H, m, CH₂C=), 2.47 (2H, m, =C-CH₂), 3.25 (2H, t, CH₂, J = 6.0 Hz), 5.2-5.5 (2H, m, CH=CH, J = 15.2 Hz).

<u>1-Bromododec-3E-ene (X)</u>. This was obtained in a similar way from 6.44 g (0.035 mole) of dodec-3E-en-1-ol (VIII) and 4.74 g (0.0175 mole) of PBr₃ with a yield of 51.9 g (60%). IR spectrum (ν , cm⁻¹): 970 (trans-CH=CH). PMR spectrum (δ , ppm): 0.84 (3H, t, CH₃), 1.05-1.4 (12H, m, CH₂, J = 6.0 Hz), 5.2-5.5 (2H, m, CH=CH, J = 15.2 Hz).

<u>Dodec-5E-enoic Acid (XV) and its n-Butyl Ester (XVI)</u>. At 75°C (nitrogen) 2.52 g (0.0158 mole) of diethyl malonate, and then 2.7 g (0.0123 mole) of 1-bromodec-3E-ene (X) were added to a solution of sodium butanolate obtained from 0.33 g (0.0143 g-mole) of sodium and 23 ml of absolute n-butanol. The reaction mixture was heated at 115°C and was stirred for 4 h, and it was then cooled to 65°C and 15 ml of 50% KOH solution was added, after which the resulting mixture was stirred at 115°C for 6 h; it was then cooled to room temperature and after 12 h a by-product was extracted from the reaction mixture with ether. The aqueous layer was acidified with concentrated HCl, and 3.6 g of a mixture of the dicarboxylic acid (XI) and its monobutyl ester (XII) was extracted from it. The mixture of compounds (XI) and (XII) (3.6 g), together with Ionol (0.02 g), was heated under nitrogen until the evolution of CO₂ had ceased (1 h). Then it was cooled to room temperature and was treated with a 10% solution of NaOH, after which diethyl ether extracted from the reaction mixture 0.4 g [12.8%, calculated on the bromide (IX)] of the n-butyl ester (XVI). IR spectra (v, cm⁻¹): 970 (trans-CH=CH), 1180, 1730 (-COOC₄H₂).

The aqueous layer, after acidification with concentrated HCl, yielded by extraction with diethyl ether 1.16 g [47.6%, calculated on the bromide (IX)] of the acid (XV). IR spectrum (ν , cm⁻¹): 970 (trans-CH=CH), 1720 (CO). Mass spectrum, m/z: 198 [M]⁺, 180 [M-H₂O]⁺.

Tetradec-5E-enoic Acid (XVII) and its Butyl Ester (XVIII). These were obtained similarly from 1.43 g (0.064 mole) of sodium, 106 ml of n-butanol, 11.29 g (0.071 mole) of diethyl malonate, and 13.5 g (0.055 mole) of 1-bromododec-3E-ene (X). The yield of the n-butyl ester (XVIII) was 2.28 g [14.7% calculated on the bromide (X)].

IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 1180, 1730 (-COOC₄H₉). PMR spectrum (δ , ppm): 0.85-0.89 (6H, m, CH₃), 1.1-1.4 (20H, m, CH₂), 1.93 (4H, m, =C-CH₂), 2.19 (2H, t, CH₂COO, J = 6.8 Hz), 3.96 (2H, t, CH₂-OCO, J = 6.5 Hz), 5.28 (2H, t, CH=CH). The yield of tetradec-5E-enoic acid (XVII) was 5.04 g [40.6%, calculated on the bromide (X)]. IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 1720 (CO). Mass spectrum, m/z: 226 [M]⁺, 208 [M-H₂O]⁺.

<u>Dodec-5E-en-1-ol (I)</u>. This was obtained as described above for the alk-3E-en-1-ols (VII) and (VIII) from 1.13 g (0.0057 mole) of dodec-5E-enoic acid (XV), 0.38 g (0.0015 mole) of its n-butyl ester (XVI), and 0.4 g (0.011 mole) of lithium tetrahydroaluminate with a yield of 0.96 g (72%) after chromatography on SiO₂ [Et₂O-hexane (1:2)], n_D^{20} 1.4538 (see [1]).

IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 3360 (OH). PMR spectrum (δ , ppm): 0.87 (3H, t, CH₃), 1.08-1.42 (12H, m, CH₂), 1.90 (4H, m, CH₂-C=), 3.52 (2H, t, CH₂O), 5.26 (2H, m, CH=CH). Mass spectrum, m/z: 184 [M]⁺.

<u>Tetradec-5E-en-1-ol (XIX)</u>. In a similar way, 1.26 g (0.0056 mole) of tetradec-5Eenoic acid (XVII), 0.82 g (0.0029 mole) of its n-butyl ester (XVIII) and 0.48 g (0.0126 mole) of lithium tetrahydroaluminate gave 1.38 g (76.6%) of the alk-5E-enol (XIX), nD^{20} 1.4538 (see [1]). IR spectrum (v, cm⁻¹): 970 (trans-CH=CH), 3340 (OH). PMR spectrum (δ , ppm): 0.85 (3H, t, CH₃), 1.1-1.4 (16H, m, CH₂), 1.92 (4H, m, CH₂-C=), 3.48 (2H, t, CH₂O, J = 6.5 Hz), 5.26 (2H, m, CH=CH). Mass spectrum, m/z: 212 [M]⁺.

Tetradec-5E-en-1-yl Acetate (II). A mixture of 1.06 g (0.005 mmole) of tetradec-5Een-1-ol (XIX), 3.3 ml of acetic anhydride, and 3.3 ml of dry pyridine was stirred at room temperature for 30 h. After the usual working up, the acetate was obtained; its yield after chromatography on silica gel [hexane-diether ether (3:1)] was 0.98 g (77.2), n_D^{20} 1.4432 (see [1]). IR spectrum (ν , cm⁻¹): 970 (trans-CH=CH), 1250, 1740 (-OCOCH₃). PMR spectrum (δ , ppm): 0.85 (3H, m, CH₃), 1.0-1.7 (16H, m, CH₂), 1.92 (3H, s, CH₃CO), 1.95 (4H, m, CH₂-C=), 3.92 (2H, t, CH₂O, J = 6.7 Hz), 5.28 (2H, m, CH=CH).

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INSECT PHEROMONES AND THEIR ANALOGUES

XXVI. SYNTHESIS OF HEXADEC-11Z-EN-1-OL AND ITS ACETATE AND HEXADEC-11Z-EN-AL - COMPONENTS OF THE PHEROMONES OF INSECTS OF THE ORDER LEPIDOPTERA

UDC 542,943.5+547.31+632.936

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Pheromone components of insects of the genera <u>Heliothis</u> and <u>Mamestra</u> have been synthesized with the use of functionally differentiated ozonolysis of cyclododecene.

An approach to the synthesis of pheromones of the alk-Z-ene series based on the transformations of the products of the functionally differentiated ozonolysis of cyclic olefins [1] had been used in the synthesis of hexadec-11Z-en-1-ol (VI) and its acetate (VII) and of hexadec-11Z-enal (VIII) - components of the sex pheromones of ecologically harmful moths of the genera Mamestra and Heliothis.

The ozonolysis of cyclododecene (I) gave a high yield of methyl 11-oxododecanoate (II) [2], which was introduced into the Wittig reaction with n-amylidenetriphenylphosphorane, leading to methyl heptadec-12-enoate (III) exclusively with the Z- configuration, as was shown by the results of GLC analysis and the ¹³C NMR spectrum.* This result on the stereo-chemistry of olefination confirmed results obtained previously for this reaction with esters of ω -formylcarboxylic acids [1].

Saponification of the ester function in (III) and subsequent oxidative decarboxylation by the action of lead tetraacetate and copper diacetate led to hexadeca-1,11Z-diene (V). Hydroboration of the diene (V) with the aid of 9-borabicyclo[3.3.1]nonane took place selectively at the terminal double bond and, after oxidation of the organoboron intermediate with a H_2O_2 -NaOH mixture, gave the desired alcohol (VI), by the acetylation of which the

^{*}The stereochemical individuality of compound (III) was shown by the single peak in its GC chromatograms obtained on various columns, including capillary columns (Shimadzu instrument).

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