INSECT PHEROMONES AND THEIR ANALOGUES

XXXVII. SYNTHESIS OF TETRADEC-11E-ENAL AND OF TETRADEC-11E-EN-1-OL AND ITS ACETATE FROM UNDECENOIC ACID

V. N. Odinokov, G. Yu. Ishmuratov, R. R. Vakhidov,
A. A. Berg, R. R. Muslukhov, and G. A. Tolstikov

UDC 547.381+542.91

A stereospecific synthesis has been achieved of tetradec-11E-enal and of tetradec-11E-en-1-ol and its acetate – components of the pheromones of many species of insects of the order Lepidoptera – from the readily available undecenoic acid, using the Knoevenagel reaction and catalytic hydroalumination.

A whole series of syntheses is known for tetradec-11E-enal (I) and the corresponding alcohol (II) and its acetate (III) [1-12], these being components of the pheromones of many species of insects of the order Lepidoptera [1-3]. Undecenoic acid (IV) has not been used for this purpose. Nevertheless, its conversion into dodec-11-enal (VI) and its conclusion in a modified [13] Knoevenagel reaction, leading to tetradeca-3,13-dienoic acid (VII) exclusively of the E-configuration opens up a convenient route to the specific synthesis of the above-mentioned compounds.

The aldehyde (VI) was obtained with a yield of 64% by the interaction with dimethylformamide of the Grignard reagent generated from undecenyl bromide (V). Confirmation of the E-configuration of the Δ^3 double bond in the product of the condensation of the aldehyde (VI) with malonic acid was provided by absorption in the regions of 970 cm^{-1} in the IR spectrum of the acid (VII) and of 985 cm^{-1} in the IR spectrum of the ester (VIII).

To obtain the desired structures, the methyl ester (VIII) was reduced to tetradeca-3E,13-dien-1-ol (IX) by the action of diisobutylaluminum hydride (DIBAH). The required deoxygenation of the alcohol (IX) was realized by treating its tosylate (X) with lithium tetrahydroaluminate. The selective hydration of the resulting tetradeca-1,11E-diene (XI) to the desired alcohol (II) was effected through an organoaluminum intermediate. The zirconium-tetrachloride-catalyzed hydroalumination of diene (XI), followed by oxidation with oxygen, gave the alcohol (II) with a yield of more than 70%, and this was converted into the acetate (III).

The oxidation of alcohol (II) with pyridinium chlorochromate led to the third of the desired compounds – the aldehyde (I). The yield of pheromone component (II) by the scheme developed amounted to 15%, calculated on the initial undecenoic acid (IV). The yields of the other two desired compounds were 14 and 12%, respectively. The stereochemical purities of the pheromones (I-III) and of the intermediate alcohol (IX) and diene (XI) were checked by capillary GLC, which confirmed the high stereoselectivity of the synthesis – the purity of all the samples exceeded 98%.

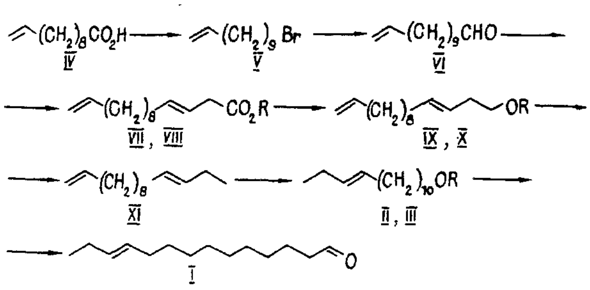
The IR spectrum of compounds (I-III) and (IX-XI) contained the intense absorption band at 980-985 cm^{-1} that is characteristic for alk-E-enes. An unambiguous confirmation of the E-geometry of the internal double bond in the diene (XI) (and, consequently, also in the other compounds synthesized) was the position of the signal of the allyl C^{10} atom at δ 32.57 ppm in the ^{13}C NMR spectrum, while for the alk-Z-enes the corresponding signal is observed in a substantially stronger field (δ 27-28 ppm) [14] (see top of following page).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film); PMR spectra were recorded on a Tesla BS-567 instrument (working frequency 100 MHz); ^{13}C NMR spectra were taken on a

---

Institute of Chemistry, Bashkir Scientific Center, Urals Branch, Russian Academy of Sciences, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 272-276, March-April, 1992. Original article submitted May 6, 1991.



R = H(II, VII, IX), Me(VIII), Ts(X), As(III)

Jeol FX-90 Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression of proton effects, the solvent being $CDCl_3$ and the chemical shifts being given on the δ scale relative to the signal of TMS (internal standard). The GLC analysis for compounds (V), (VI), and (VIII) was conducted on a Chrom-5 instrument with the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.2 mm) at a working temperature of 50-300°C for compounds (I)-(III), (IX) and (XI), and on a Shimadzu instrument with the stationary phase PEG-20M in a 25 m × 0.2 m [sic] glass capillary column at a working temperature of 80-180°C, the carrier gas being helium. The results of elementary analysis corresponded to the calculated figures.

Dodec-11-enal (VI). The Grignard reagent prepared from 6.2 g ($26.6 \cdot 10^{-3}$ mole) of 1-bromoundec-10-ene (V) (obtained from the acid (IV) as described in [15], yield 73%, n_D^{22} 1.4505) and 0.7 g ($28.8 \cdot 10^{-3}$ g-atom) of magnesium in 25 ml of absolute THF was added dropwise (Ar. 0°C) to a solution of 2.0 g ($27.5 \cdot 10^{-3}$ mole) of DMFA in 17.5 ml of absolute THF. The reaction mixture was stirred at room temperature for 2 h and it was then cooled to 5°C, acidified with 5% HCl, and extracted with diethyl ether (3 × 70 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, pentane—diethyl ether (10:1)]. This gave 3.1 g (64%) of the aldehyde (VI), n_D^{18} 1.4478, IR and PMR spectra identical with those given in [16].

Methyl Tetradeca-3E,13-dienoate (VIII). Over 15 min, 2.3 g ($12.5 \cdot 10^{-3}$ mole) of the aldehyde (VI) was added dropwise to a mixture of 4.0 g ($38.4 \cdot 10^{-3}$ mole) of malonic acid, 1.6 mg ($0.0125 \cdot 10^{-3}$ mole) of piperidine acetate, and 10.2 ml of absolute p-xylene heated to the boil in a flask with a Dean-Stark trap, and the reaction mixture was boiled until the evolution of water and CO_2 had ceased (3-4 h) and it was then cooled to room temperature, diluted with 50 ml of diethyl ether, washed with water (2 × 10 ml), dried with $MgSO_4$, and evaporated. The residue (2.03 g) of tetradeca-3E,13-dienoic acid (VII) [IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$), 970 (E-CH=CH), 1710, 2400-3600 (CO_2H)] was treated with 0.2 g of TsOH in 15 ml of absolute methanol, and the mixture was left at room temperature for 24 h. Then the solvent was distilled off, the residue was dissolved in 100 ml of diethyl ether, and the solution was washed successively with saturated solutions of $NaHCO_3$ and of NaCl, and was dried with $MgSO_4$ and evaporated. The residue was chromatographed [SiO_2, hexane—diethyl ether (9:1)]. This gave 1.86 g (62%) of the ester (VIII), n_D^{18} 1.4540. IR spectrum (ν, cm^{-1}): 925, 1010, 3090 ($CH{=}CH_2$), 985 (E-CH=CH), 1745 (C=O). PMR spectrum (100 MHz, $CDCl_3$): 1.15-1.7 (m, 12H, CH_2), 1.86-2.18 (m, 4H, H-5, H-12), 3.03 (d, 2H, J = 4.5 Hz, H-2), 3.68 (s, 3H, CO_2CH_3), 4.84-5.12 (m, 2H, H-14), 5.46-6.04 (m, 3H, H-3, H-4, H-13).

Tetradeca-3E,13-dien-1-ol (IX). To a solution of 1.1 g ($4.62 \cdot 10^{-3}$ mole) of ester (VIII) in 20 ml of absolute diethyl ether was added (Ar, −20°C) 3.0 ml of a 73% solution of DIBAH ($13.2 \cdot 10^{-3}$ mole) in toluene; the mixture was stirred for 1.5 h and was then warmed to 0°C, and 2.8 ml of water was added dropwise. The reaction mixture was stirred at room temperature for 2 h and was then extracted with diethyl ether (3 × 100 ml). The combined extracts were washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. This gave 0.9 g (93%) of the alcohol (IX) with a purity, according to capillary GLC, of not less than 98%, n_D^{22} 1.4602. IR spectrum (ν, cm^{-1}): 925, 1010, 3090 ($CH{=}CH_2$), 985 (E-CH=CH), 3200-3600 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.14-1.66 (m, 12H, CH_2), 1.85-2.16 (m, 4H, H-5, H-12), 2.2-2.38 (m, 2H, H-2), 3.62 (t, 2H, J = 6.2 Hz, H-1), 4.85-5.13 (m, 2H, H-14), 5.36-6.04 (m, 3H, H-3, H-4, H-13).

1-Tosyloxytetradeca-3E,13-diene (X). In portions, 3.38 g ($17.7 \cdot 10^{-3}$ mole) of TsCl was added at −5-0°C to a solution of 1.86 g ($8.9 \cdot 10^{-3}$ mole) of the alcohol (IX) in 5.1 ml of dry pyridine, and the mixture was stirred at −5°C for 6 h and kept at 0°C for 12 h, and it was then poured onto ice (3 g) and was extracted with diethyl ether (3 × 50 ml). The extract was washed successively with 10% HCl and saturated solutions of $NaHCO_3$ and of NaCl, and was dried with $MgSO_4$ and evaporated. This gave 3.12 g (97%) of the tosylate (X). IR spectrum (ν, cm^{-1}): 930, 1010, 3090 ($CH{=}CH_2$), 985 (E-CH=CH), 1190, 1375, 1605 (OTs).

Tetradeca-1,11E-diene (IX). A solution of 2.1 g ($5.77 \cdot 10^{-3}$ mole) of the tosylate (X) in 2 ml of absolute diethyl ether was added dropwise (Ar, 0°C) to a suspension of 0.33 g ($8.65 \cdot 10^{-3}$ mole) of $LiAlH_4$ in 3 ml of absolute diethyl ether, and the mixture was stirred for 1.5 h, after which 3 ml of water was added at the same temperature and extraction was carried out with pentane (3 × 50 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$ and evaporated. The residue was chromatographed (neutral Al_2O_3, pentane). This gave 0.92 g (82%) of the diene (XI) with a purity, according to capillary GLC, of not less than 98%, n_D^{21} 1.4422.

IR spectrum (ν, cm^{-1}): 930, 1010, 3090 (CH=CH), 980 (E-CH=CH), 1645. PMR spectrum, (100 MHz, $CDCl_3$): 0.96 (t, 3H, J = 7 Hz, H-14), 1.15-1.65 (m, 12H, CH_2), 1.85-2.2 (m, 6H, CH_2), 4.85-5.15 (m, 2H, H-1), 5.36-5.54 (m, 2H, H-11, H-12), 5.6-6.0 (m, 1H, H-2). ^{13}C NMR spectrum (22.5 MHz, $CDCl_3$): 114.04 (t, C-1), 139.17 (d, C-2), 33.81 (t, C-3), 29.63 (t, C-4), 29.18-29.44 (t, C-5, C-6, C-7, C-8), 28.98 (t, C-9), 32.57 (t, C-10), 129.31 (d, C-11), 131.79 (d, C-12), 25.59 (t, C-13), 13.97 (C-14).

Tetradec-11E-en-1-ol (II). At room temperature, 1.03 ml of a 73% solution of DIBAH ($4.12 \cdot 10^{-3}$ mole) in toluene was added to a solution of 0.8 g ($4.1 \cdot 10^{-3}$ mole) of the diene (XI) and 0.029 g of $ZrCl_4$ in 4.1 ml of absolute hexane, and the mixture was stirred for 7 h; dried air was bubbled through (0°C, 1 h; 20°C, 1 h) and then oxygen (60°C, 4 h), after which the reaction mixture was cooled to 0°C, 3 ml of 5% HCl was added, and it was stirred for 0.5 h and was extracted with diethyl ether (3 × 50 ml). The extract was washed successively with saturated solutions of $NaHCO_3$ and of NaCl, and was dried with $MgSO_4$ and evaporated. The residue was chromatographed [SiO_2, hexane—diethyl ether (7:3)], and 0.62 g (71%) of the alcohol was obtained with a purity, according to capillary GLC of not less than 98%, n_D^{20} 1.4560, its IR and PMR spectra being identical with those given in [11].

Tetradec-11E-en-1-yl Acetate (III). To 0.51 g ($2.4 \cdot 10^{-3}$ mole) was added 3 ml of a mixture (2:3) of acetic anhydride and pyridine, and the mixture was left at room temperature for 24 h and was then diluted with 100 ml of CH_2Cl_2 and was washed successively with 10% HCl and saturated solutions of $NaHCO_3$ and of NaCl, dried, and evaporated. The residue was chromatographed [SiO_2, hexane—diethyl ether (10:1)]. This gave 0.56 g (92%) of the acetate (III) with a purity, according to capillary GLC of not less than 98%, n_D^{20} 1.4478. Its IR and ^1H and ^{13}C NMR spectra were identical with those given in [11].

Tetradec-11E-enal (I). With stirring (Ar, 20°C) a solution of 0.39 g ($1.85 \cdot 10^{-3}$ mole) of alcohol (II) in 1 ml of CH_2Cl_2 was added to a suspension of 0.6 g of pyridinium chlorochromate in 7 ml of redistilled CH_2Cl_2. The reaction mixture was stirred for 2 h, and then it was diluted with 50 ml of diethyl ether and filtered through a layer (5 cm) of SiO_2. The residue on the filter was washed with 50 ml of diethyl ether, and the solution was dried with $MgSO_4$ and evaporated. The evaporation residue was chromatographed [SiO_2, hexane—diethyl ether (4:1)]. This gave 0.29 g (76%) of the aldehyde (I), with a purity according to capillary GLC of not less than 98%, n_D^{20} 1.4485, its IR and PMR spectra being identical with those given in [11].

LITERATURE CITED

1. H. J. Bestmann and O. Vostrovsky, Chemie der Pflantzenschutz- und Schädlings-Bekämpfungsmittel, Springer Verlag, Berlin, Vol. 6 (1981), p. 29.
2. R. Rossi, Synthesis, No. 12, 817 (1977).
3. C. A. Henrick, Tetrahedron, 33, 1846 (1977).
4. T. M. Fyles, C. C. Leznoff, and J. Weatherston, J. Chem. Ecol., 4, No. 1, 109 (1978).
5. L. I. Zakharkin and E. A. Petrushkina, Zh. Org. Khim., 18, No. 8, 1623 (1982).
6. L. I. Zakharkin and V. V. Guseva, Khim. Prir. Soedin., No. 6, 776 (1984).
7. L. Pop, I. Oprean, A. Barabas, and F. P. Hodosan, J. Prakt. Chem., 328, No. 5-6, 867 (1986).
8. H. Ishibashi, H. Komatzu, and M. Ikeda, J. Chem. Res., Synop., No. 9, 296 (1987).
9. V. Ratovelomanana and G. Linstrumelle, Synth. Commun., 14, No. 2, 179 (1984).
10. Han-Dong Li, Yan-Neng Deng, Han-Sheng Xu, Li Tao, and Hui-Sheng Qu, Yousi Huaxue, Chinese J. Org. Chem., 8, No. 2, 167 (1988).

11. H. C. Brown, H. D. Lee, and S. U. Kulkarni, J. Org. Chem., 51, No. 26, 5282 (1986).
12. T. H. Chan and K. Koumaglo, Tetrahedron Lett., 27, No. 8, 883 (1986).
13. N. Ragoussis, S. A. Vioryl, and K. Kato, Tetrahedron Lett., 28, No. 1, 93 (1987).
14. V. N. Odinokov, R. S. Bakeeva, R. I. Galeeva, V. R. Akhunova, Ya. G. Mukhtarov, G. A. Tolstikov, L. M. Khalilov, and A. A. Panasenko, Zh. Org. Khim., 15, No. 10, 2017 (1979).
15. Nguen Kong Khao, M. V. Mavrov, and É. P. Serebryakova, Bioorg. Khim., 14, No. 2, 250 (1988).
16. R. A. Amos and J. A. Katzenellenbogen, J. Org. Chem., 43, No. 4, 560 (1978).

SYNTHESIS OF HEXADEC-9Z-ENAL – ONE OF THE COMPONENTS OF THE SEX PHEROMONE OF Heliothis armigera

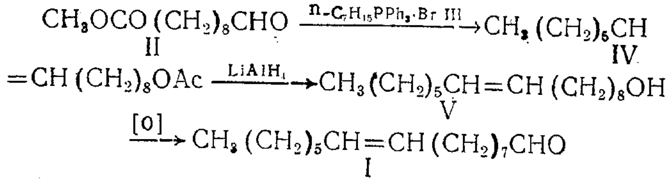
T. Dzhumakulov and M. M. Kadyrova

UDC 547.996:632.936+2

Hexadec-9Z-enal – a component of the sex pheromone of the cotton bollworm *Heliothis armigera* – has been obtained by a three-stage synthesis from 9-acetoxynonanal and n-heptyltriphenylphosphonium bromide followed by reduction and oxidation.

Hexadec-9Z-enal (I) is one of the components of the pheromone of the cotton bollworm – the principal pest of the cotton plant [1]. The traditional methods for synthesizing the aldehyde (I) are based on the alkylation of lithium octynylide with 2-(8-chlorooctyloxy)- or 2-(8-bromooctyloxy)tetrahydropyran, followed by hydrolysis and then the hydrogenation of the resulting hexadec-9-yn-ol to hexadec-9Z-en-1-ol and the conversion of the latter into (I) [2].

We have carried out a three-stage synthesis of the aldehyde (I) that permits the performance of the successive reactions in one flask, including the condensation of 9-acetoxynonanal (II) with n-heptyltriphenylphosphonium bromide (III) under the conditions given in [3].



$$\underset{\text{II}}{CH_3OCO(CH_2)_8CHO} \xrightarrow{n\text{-}C_7H_{15}PPh_3\cdot Br\ \text{III}} \underset{\text{IV}}{CH_3(CH_2)_5CH}$$
$$=CH(CH_2)_8OAc \xrightarrow{LiAlH_4} \underset{\text{V}}{CH_3(CH_2)_5CH=CH(CH_2)_8OH}$$
$$\xrightarrow{[0]} \underset{\text{I}}{CH_3(CH_2)_5CH=CH(CH_2)_7CHO}$$

The initial 9-acetoxynonanal (II) was obtained by the oxidation of 9-acetoxynonan-1-ol with pyridinium chlorochromate in methylene chloride [4]. The reaction of aldehyde (II) with the phosphonium salt (III) gave hexadec-9Z-enyl acetate (IV), which was reduced with lithium tetrahydroaluminate to hexadec-9Z-en-1-ol (V). Oxidation of the latter with pyridinium chlorochromate gave hexadec-9Z-enal (I).

The isomeric purity of the aldehyde (I), determined by gas-liquid chromatography (GLC), was not less than 97%.

EXPERIMENTAL

IR spectra were taken on a Specord 75 spectrometer in CCl_4. The PMR spectra of the substances under investigation in CCl_4 were obtained relative to HMDS on a Varian MAT 311 in-

---

A. S. Sadykov Institute of Bioorganic Chemistry, Uzbekistan Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 276-277, March-April, 1992. Original article submitted July 15, 1991; revision submitted November 19, 1991.

0009-3130/92/2802-0240$12.50 © 1992 Plenum Publishing Corporation