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CHEMICAL CONVERSION OF 9-TETRADECEN-1-OL ACETATES TO 3,13-OCTADECADIEN-1-OL ACETATES, SEX ATTRACTANTS FOR MALE CLEARWING MOTHS (LEPIDOPTERA: SESIIDAE)

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Abstract—Males of many species of clearwing moths are attracted by one of the geometrical isomers of 3,13-octadecadien-1-ol acetate or by a mixture of isomers. The synthesis of (*E,Z*)-, (*E,E*)-, and (*Z,E*)-3,13-octadecadien-1-ol acetate is described starting with the (*Z*)- and (*E*)-9-tetraceden-1-ol acetates, which are commercially obtainable.

Key Words—Sex pheromone, attractants, 9-tetradecen-1-ol acetate, 3,13-octadecadien-1-ol acetate, clearwing moth, Lepidoptera, Sesiidae, synthesis.

INTRODUCTION

Males of many species of clearwing moths (Lepidoptera: Sesiidae) are attracted by a 3,13-octadecadien-1-ol acetate (3,13-ODDA) or by a mixture of two or more of its geometrical isomers (Nielsen et al., 1975, 1978; Nielsen and Purrington, 1978; Barry et al., 1978; Karandinos et al., 1977; Yaginuma et al., 1976; Tumlinson et al., 1974). Recently we found that commercially obtained (*Z,Z*)-3,13-ODDA containing small amounts of its geometrical isomers is very attractive to the male clearwing moth *Synanthedon myopaeformis* (Borkhausen) (Voerman et al., 1978).

In order to study the influence of the *E,Z*, *Z,E*, and *E,E* isomers on the attractivity of (*Z,Z*)-3,13-ODDA for *S. myopaeformis*, we had to synthesize them.

A synthetic route to all four isomers was indicated by Tumlinson et al. (1974) and was described in detail by Doolittle et al. (1978). They used octamethylene chloroiodide as starting material. Underhill et al. (1978) prepared (*Z*,*Z*)-3,13-ODDA beginning with the condensation of 1-bromo-9-tetradecyne with 2-(3-butynyloxy)tetrahydropyran. No details were given. Uchida et al. (1978) described the synthesis of (*Z*,*Z*)- and (*E*,*Z*)-3,13-ODDA. Their overall yields were rather low.

In this paper, the conversion of (*Z*)-9-tetradecen-1-ol acetate to (*E*,*Z*)-3,13-ODDA and that of (*E*)-9-tetradecen-1-ol acetate to (*E*,*E*)- and (*Z*,*E*)-3,13-ODDA is described. The 9-tetradecen-1-ol acetates are attractive to several species of moths, singly or in combination with another compound (Mayer and McLaughlin, 1975) and are commercially obtainable.

METHODS AND MATERIALS

The progress of all reactions was followed, and all products checked, by gas-liquid chromatography (Voerman and Rothschild, 1978). The end-products were ultimately purified by liquid chromatography through a column packed with a silver-loaded resin (glass column, 200 × 1.6 cm, packed with Lewatit SP 1080, 170-200 mesh, Ag^+ form, eluent methanol, temperature 25–28° C) (Houx et al., 1974). Purity was also checked with HPLC (Houx and Voerman, 1976; Voerman, 1978).

The starting compounds (*Z*)-9- and (*E*)-9-tetradecen-1-ol acetate were bought from Farchan Division,Chemical Samples Co. (Willoughby, Ohio 44094), purity 95%, estimated by HPLC. The reaction schemes are shown in Figures 1 and 2.

Synthesis of (E,Z)-3,13-Octadecadien-1-ol Acetate

(Z)-9-Tetradecen-1-ol (I). Overnight, 17.8 g (*Z*)-9-tetradecen-1-ol acetate (0.070 mol) was stirred at room temperature in 100 ml of a 2% solution

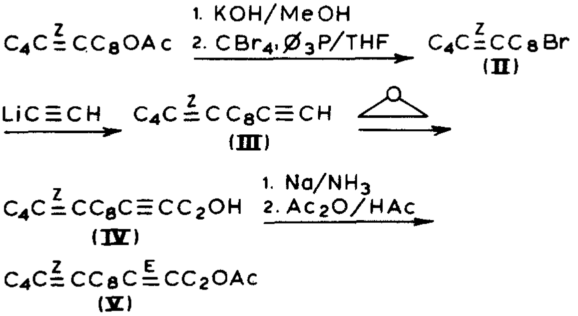


FIG. 1. Chemical conversion of (*Z*)-9-tetradecen-1-ol acetate to (*E*,*Z*)-3,13-octadecadien-1-ol acetate (V).

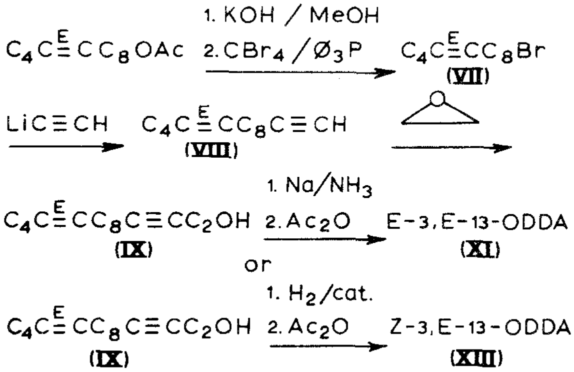


FIG. 2. Chemical conversion of (*E*)-9-tetradecen-1-ol-acetate to (*E*,*E*)- and (*Z*,*E*)-3,13-octadecadien-1-ol acetate (XI and XIII).

of KOH in MeOH. Then most of the solvent was removed at reduced pressure in a rotary evaporator; 200 ml 20% NaCl solution was added, and the water layer extracted with 5 × 50 ml hexane. The hexane extract was washed with 20% NaCl solution in water until neutral and dried over Na_2SO_4, giving I quantitatively after evaporation of the hexane in a rotary evaporator.

(*Z*)-*9-Tetradecenyl Bromide* (*II*). To 14.8 g (0.070 mol) of crude I in 20 ml dry THF were added 29.9 g (0.090 mol) CBr_4 in 15 ml dry THF and then slowly 23.6 g (0.090 mol) triphenylphosphine in 50 ml dry THF. The mixture was stirred mechanically. The slightly exothermic reaction was complete after about 1 hr (Hooz and Gilani, 1968). Stirring was continued for 3/4 hr after addition of 10 ml MeOH to destroy excess reagents. Then the solvent was removed by rotary evaporation and the residue chromatographed through Al_2O_3 (column 2 × 40 cm, packed with 30 g Al_2O_3) with hexane as mobile phase. The eluate was distilled, main fraction 17.5 g (90.9%), bp 93°C/0.08 mm, n_D^{25} 1.4695.

(*Z*)-*11-Hexadecen-1-yn* (*III*). Over 3/4 hr, 17.5 g (0.064 mol) of II in 60 ml HMPT was added to 6.9 g (0.08 mol) lithium acetylide ethylene diamine complex in 40 ml dry THF. During addition, the mixture was well stirred and the temperature was kept below 17°C. After stirring overnight at room temperature, it was poured into a mixture of 300 ml ice water and 60 g NaCl. The water layer was extracted with 5 × 50 ml hexane, washed with 20% NaCl until neutral, and dried over Na_2SO_4. Distillation gave 10.9 g (77.9%) of III, bp 73°C/0.03 mm, n_D^{25} 1.4530 [Doolittle et al. (1978) found bp 70°C/0.005 mm, n_D^{25} 1.4526.]

(*Z*)-*13-Octadecen-3-yn-1-ol* (*IV*). To 10.9 g (0.050 mol) of III in 80 ml dry THF was added, at 0°C under a weak stream of N_2, 37 ml of a hexane solution of butyllithium (1.6 M). After stirring was continued 1 hr at room temperature, 7 ml ethylene oxide (6.2 g, 0.141 mol) dissolved in 40 ml cold HMPT was added at 0°C in a cold room. After stirring overnight at room temperature, the mixture was poured into a mixture of 400 ml ice water and 100 g NaCl. The resulting mixture was extracted with hexane, the extract washed with 20% NaCl until neutral, and dried over Na_2SO_4. Distillation after removing of the solvent by rotary evaporation gave a yellow oil, 10.5 g (80.2%), bp 124°C/0.03 mm, n_D^{25} 1.4730 [Doolittle et al. (1978) report bp 132-140°C/0.04 mm; Uchida et al. (1978) report bp 148-150°C/0.6 mm, n_D^{25} 1.4708.]

(E,Z)-3,13-Octadecadien-1-ol Acetate (V). A solution of 10.5 g (0.040 mol) of IV in 200 ml dry THF was slowly added to 3.7 g (0.161 mol) sodium dissolved in 300 ml NH_3. After stirring overnight, 14% of IV was still present. Another 100 ml dry THF was added and stirring was continued for 4 days. From time to time, some sodium dissolved in NH_3 was added to keep the mixture blue. Then the NH_3 was allowed to evaporate, 100 ml saturated NH_4Cl and 100 ml 20% NaCl were added, and the aqueous layer was extracted with hexane. The extract was washed with 20% NaCl and dried over Na_2SO_4. After removing the solvent, 12.4 g of an oil remained, still containing 2% of IV.

To this oil, 10 ml HAc and 10 ml Ac_2O were added. After standing for two days, the mixture was warmed for a few hours on a water bath and poured into 100 ml ice water. The mixture was stirred for a while and then extracted with hexane. The hexane extract was washed until neutral, dried over Na_2SO_4 and distilled. Main fraction 10.0 g (81.3%), bp 121°C/0.01 mm, n_D^{25} 1.4575 [Doolittle et al. (1978) found bp 135-140°C/0.03 mm, n_D^{25} 1.4569; Uchida et al. (1978) found n_D^{24} 1.4570.]

The overall yield from I to V was 46.2%.

Pure V was obtained by liquid chromatography through a column packed with a silver-loaded resin, n_D^{25} 1.4574. Calculated for $C_{20}H_{36}O_2$: C 77.9; H 11.8. Found: C 78.3; H 11.9.

Synthesis of (E,E)- and (Z,E)-3,13-Octadecadien-1-ol Acetate

(E)-9-Tetradecen-1-ol (VI). As described for the preparation of I, 48.3 g (0.19 mol) (*E*)-9-tetradecen-1-ol acetate was treated with a 2% solution of KOH in MeOH, giving VI quantitatively.

(E)-9-Tetradecenyl Bromide (VII). To a mechanically stirred solution of 40.3 g (0.19 mol) of VI in 50 ml dry THF were added 81.3 g (0.245 mol) CBr_4 dissolved in 40 ml dry THF and then dropwise a solution of 64.2 g (0.245 mol) triphenylphosphine in 110 ml dry THF. After the reaction was complete, excess reagents were destroyed by adding 5 ml MeOH, and stirring was continued for a few hours. The mixture was worked up as described for II. The resulting crude oil was chromatographed a second time through 15 g Al_2O_3 before distillation. Main fraction 47.6 g (91%), bp 92°C/0.03 mm, n_D^{25} 1.4690.

(E)-11-Hexadecen-1-yn (VIII). A solution of 59.9 g (0.22 mol) of VII in 210 ml HMPT was added to 24.8 g (0.27 mol) lithium acetylide ethylene diamine complex in 140 ml dry THF at a temperature of 10–15°C. The reaction mixture was worked up as for the preparation of III. Distillation gave a main fraction of 42.7 g (92.4%), bp 70°C/0.02 mm, n_D^{25} 1.4520.

(E)-13-Octadecen-3-yn-1-ol (IX). To 42.7 g (0.194 mol) of VIII in 250 ml dry THF was added under nitrogen at −5°C 140 ml of a hexane solution of butyllithium (1.6 M). After stirring some time at room temperature, 22.5 ml (20 g, 0.455 mol) ethylene oxide dissolved in 125 ml HMPT was added at 0°C in a cold room. Then the mixture was allowed to warm up and stirring was continued overnight at room temperature. The mixture was worked up as described for synthesis of IV. Distillation gave 43.2 (84.4%) of IX, bp 124°C/0.02 mm, n_D^{25} 1.4703.

(E,E)-3,13-Octadecadien-1-ol (X). A solution of 21.6 g (0.082 mol) of IX in 300 ml dry THF was added to 600 ml NH_3. Small pieces of sodium were added (6.9 g, 0.3 mol). This mixture was stirred for 7 days. From time to time, some sodium was added to keep the solution blue and some NH_3 to compensate for evaporation. Then it was worked up as described for V, giving 21.2 g of the oil (X), still containing about 10% of IX. Half of this oil was distilled, main fraction 8.8 g (80.7%), bp 116°C/0.01 mm, n_D^{25} 1.4663. The 10% IX in the distillate could be removed by argentation chromatography. Pure X has n_D^{25} 1.4660.

(E,E)-3,13-Octadecadien-1-ol Acetate (XI). The other half of the crude X, 10.6 g (0.040 mol), was acetylated with 10 ml HAc and 10 ml Ac_2O as described for V. Distillation gave 9.0 g (71.4%) of XI, bp 118°C/0.01 mm, n_D^{25} 1.4560 [Doolittle et al. (1978) report bp 129–132°C/0.07 mm.]

The overall yield from VI to XI was 50.7%.

Pure XI was obtained by liquid chromatography, n_D^{25} 1.4567. Calculated for $C_{20}H_{36}O_2$; C 77.9; H 11.8; found: C 78.1; H 11.7

(Z,E)-3,13-Octadecadien-1-ol (XII). To 2.5 g $Ni(OAc)_2 \cdot 4H_2O$ in 90 ml EtOH was added, under H_2, 10 ml of a $NaBH_4$ solution (prepared by filtering the solution resulting from 1 g $NaBH_4$, 24 ml EtOH, and 1.25 ml 2 N NaOH) (Brown and Ahuja, 1973a,b). After the hydrogen had ceased to evolve, 1.3 ml 1,2-diaminoethane and 21.6 g (0.082 mol) of IX were added. With vigorous stirring, 1887 ml H_2 was taken up. Then the reaction stopped. The mixture was filtered into 700 ml 20% NaCl, the water layer extracted with ether, the extract washed with 20% NaCl, and dried over Na_2SO_4. After removing the ether with a rotary evaporator, 21.3 g oil remained, of which 10.6 g was distilled, main fraction 9.5 g (87.2%), bp 115°C/0.005 mm, n_D^{25} 1.4667, which was further purified by argentation chromatography, giving pure XII, n_D^{25} 1.4668.

(Z,E)-3,13-Octadecadien-1-ol Acetate (XIII). The other half of crude XII, 10.6 g (0.040 mol) was acetylated as for XI. Distillation gave XIII,

9.8 g (79.9%), bp 115°C/0.005 mm, n_D^{25} 1.4560 [Doolittle et al. (1978) report bp 133-135°C/0.25 mm, n_D^{25} 1.4572.]

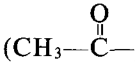
The overall yield from VI to VIII was 56.7%.

The product was further purified by liquid chromatography giving pure XIII, n_D^{25} 1.4574. Calculated for $C_{20}H_{36}O_2$: C 77.9; H 11.8; found: C 78.3; H 11.9.

RESULTS

Purified commercial (*Z,Z*)-3,13-ODDA (from Farchan Division) had n_D^{25} 1.4580. The four geometrical isomers could be separated on a stainless-steel column (25 × 0.46 cm) packed with 10-μm Nucleosil 10 SA (Ag^+). Mobile phase: methanol, 0.8 ml/min. Pressure: 32 kg/cm^2. Column temperature: 7°C. (Houx and Voerman, 1976; Voerman, 1979).

Compounds V, XI, and XIII had consistent mass spectra.

[^{1}H]Nuclear magnetic resonance (NMR) spectra (Hitachi Perkin-Elmer R-24B and Varian XL-100-15 spectrometers, $CDCl_3$ solutions, tetramethylsilane as internal reference) of these acetates were very similar. Chemical shifts, δ: 0.89 broad t (CH_3); 1.29 broad s (16 H); 1.70-2.40 broad (6H); 2.01 s  ($CH_3—\overset{O}{\overset{\|}{C}}—$); 2.30 q [2H, $J = 6$ Hz: CH_2 group at position 2, also coupled with H at carbon atom number 3 (proved by decoupling experiments)]. In XIII this CH_2 group absorbs at 2.36; 4.05 t (2H, $J = 6$ Hz: $—CH_2—O$); 5.00-5.80 m (4H: olefinic H, slightly different patterns in V, XI, and XIII).

The [^{1}H]NMR spectra of the alcohols X and XII agreed with those of the acetates V, XI, and XIII except the chemical shifts of the CH_2 group at position 2, δ ppm: 2.25 q (in X); 2.30 q (in XII) and $—CH_2—O—$ 3.60 t (2H, $J = 6$ Hz).

Infrared spectra (Hitachi EPI-G3 spectrometer, solutions in $CHCl_3$) of the acetates V, XI, and XIII showed typical absorption bands at 1735 cm^{-1} (CO stretching) and 971 cm^{-1} (CH deformation, most intense in XI). The alcohols X and XII showed typical bands at 3600 cm^{-1} (OH stretching) and 971 cm^{-1} (CH deformation, most intense in X).

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