

PHEROMONES OF INSECTS AND THEIR ANALOGS.

LII. SYNTHESIS OF DODEC-9-EN-1-YL AND TETRADEC-11-EN-1-YL ACETATES FROM THE PRODUCTS OF THE PARTIAL OZONOLYSIS OF CYCLOOCTA-1Z,5Z-DIENE AND CYCLODECA-1E,5Z-DIENE

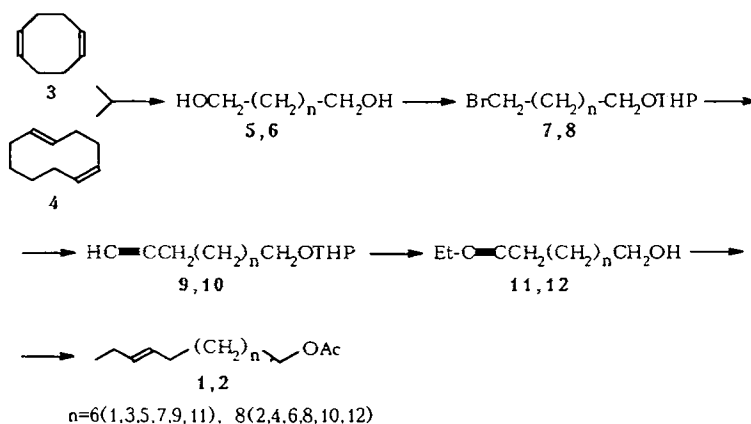
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*A new approach to the synthesis of octane-1,8- and decane-1,10-diols based on the partial ozonolysis of cyclic oligomers has been developed.*

Dodec-9E-en-1-yl acetate (1) and the alcohol corresponding to it have been identified as components of the sex pheromone of the grape moth *Sparganothis pilleriana* [1], while tetradec-11E-1-yl acetate (2) is the sex pheromone of the beet webworm *Loxostege sticticalis* [2]. The acetylene route is usually used for the synthesis of pheromones having the structure of alk-E-en-1-ols [3-5], but other approaches to the synthesis of pheromones (1) and (2) are also known [6-10]. In the majority of cases, key synthons for (1) and (2) are octane-1,8-diol (5) and decane-1,10-diol (6), respectively.

The partial ozonolysis of cyclic oligomers of 1,3-dienes [11, 12] has recommended itself as an effective approach to the synthesis of  $\alpha,\omega$ -bifunctional aliphatic compounds, opening up new possibilities in the synthesis of pheromones and juvenoids [13, 14]. According to this approach, the conversion of cyclic di- and trienes into the corresponding  $\alpha,\omega$ -bifunctional saturated compounds with the same number of carbon atoms is carried out in three operations: partial ozonolysis of a cyclooligomer at one multiple bond, catalytic hydrogenation of the double bonds remaining in the ozonolysis product, and transformation of the terminal groups into acid, aldehyde, or alcohol functions [15, 16].



This route has advantages over an alternative also involving three operations (selective hydrogenation of a cyclodi- or triene, ozonolysis of the cyclic monoene obtained, and transformation of the terminal functional groups); however, here, at the stage of the hydrogenation of the cyclooligomer complications arise in achieving high selectivity. By means of the approach

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developed, starting from cycloocta-1Z,5Z-diene (3) and cyclodeca-1E,5Z-diene (4), we have synthesized the required dienes (5) and (6), the subsequent transformation of which through the intermediate compounds (7-12) has led to the desired pheromones (1) and (2).

## 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);  $^{13}\text{C}$  NMR spectra were taken on a YCOL FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression for protons, using  $\text{CDCl}_3$  as solvent and TMS as internal standard. GLC analysis was conducted on a Chrom-5 instrument with the stationary phase SE-30 liquid (5%) on Chromaton N-AW-DMCS (0.16-0.2 mm), working temperature 50-300°C, or, for compounds (1) and (2) on a Shimadzu instrument with the stationary phase PEG-20M in a glass capillary column 0.2 mm  $\times$  25 m, working temperature 80-180°C, carrier gas helium.

**Octane-1,8-diol (5) and Decane-1,10-diol (6).** At 5°C an ozone-oxygen mixture was passed at the rate of 30 ml/h (the productivity of the ozonizer being 50 mmole of  $\text{O}_3/\text{h}$ ) through a solution of 50 mmole of the appropriate oligomer (5.4 g of (3) or 6.8 g of (4)) in 150 ml of cyclohexane containing 4 ml of methanol until 2.16 g of ozone had been absorbed (54 min). The reaction mixture was flushed with nitrogen and the solvent was decanted from the ozonide that had deposited; this was dissolved in 75 ml of methanol, and, after the addition of 0.2 g of catalyst (5% Pd/C), the solution was kept in a hydrogen atmosphere (20 atm, 25°C) in an oscillating autoclave for 20 h and was then filtered. With stirring at 15-20°C, 1.4 g of sodium tetrahydroborate was added in portions to the filtrate and the mixture was stirred for another 5 h and was left at room temperature for 15 h; it was then diluted with 20 ml of  $\text{H}_2\text{O}-\text{AcOH}$  (10:1), stirred for 3 h, and filtered, the filtrate was evaporated, the residue was dissolved in 50 ml of  $\text{Et}_2\text{O}$ , the resulting solution was filtered, and the deposit was washed with 100 ml of  $\text{Et}_2\text{O}$ . The ethereal solutions were combined and washed with saturated NaCl solution ( $3 \times 20$  ml), dried with  $\text{MgSO}_4$ , and evaporated. This gave 5.7 g (78%) of the diol (5), mp 60-62°C (see [17]) or 6.5 g (75%) of the diol (6), mp 70-72°C (see [18]).

**1-Bromo-8-(2-tetrahydropyranyloxy)octane (7) and 1-Bromo-10-(2-tetrahydropyranyloxy)decane (8).** A mixture of 7.3 g (50 mmole) of diol (5) or 8.7 g (50 mmole) of diol (6) and 10 ml (60 mmole) of 48% HBr was heated for 60 h while being extracted continuously with heptane, which was then evaporated. In each experiment the residue was dissolved in 45 ml of  $\text{Et}_2\text{O}$ ; to this solution were added 0.14 g of TsOH and 5.4 ml of dihydropyran that had been kept over NaOH and redistilled over Na, and the resulting mixture was stirred for 2 h and was left at room temperature for 24 h, after which it was washed successively with saturated solutions of  $\text{NaHCO}_3$  and NaCl, dried over  $\text{MgSO}_4$ , and evaporated. This gave 10 g (74%) of compound (7) or 11.9 g (74.5%) of compound (8), their IR and PMR spectra being identical with those given in [19] and [18], respectively.

**Dodec-9-yn-1-ol (11) and Tetradec-11-yn-1-ol (12).** At -35°C, with stirring, 0.2 g of finely cut lithium and 0.03 g of  $\text{FeCl}_3$  were added to 90 ml of redistilled liquid ammonia and the reaction mixture was stirred until a permanent gray color had appeared; then 4.5 g of compound (9) or 5.2 g of compound (10) (obtained by the procedure of [20]) was added, the mixture was stirred for 1 h, and a solution of 2.7 ml of ethyl bromide in 5 ml of abs. THP and 5 ml of abs. DMSO was added over 5 min. After stirring at -40°C for 2 h, the ammonia was allowed to evaporate, and the residue was treated with 30 ml of water and extracted with hexane ( $3 \times 50$  ml). The combined extracts were washed successively with 10% HCl and with saturated solutions of  $\text{NaHCO}_3$  and NaCl, dried with  $\text{MgSO}_4$ , and evaporated. The residue from each experiment was dissolved in 40 ml of methanol, 4 ml of water and 0.9 g of TsOH were added, and the mixture was stirred at room temperature for 20 h, after which the methanol was distilled off and the residue was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 100$  ml): the usual working up and chromatographic purification ( $\text{SiO}_2$ ,  $n\text{-C}_6\text{H}_{12}-\text{Et}_2\text{O}$  (3:1)) gave 2.9 g (85%) of the aglycon (11) or 3.0 g (86%) of the aglycon (12),  $n_D^{20}$  1.4645, IR and PMR spectra identical with those given in [21].

**Dodec-9E-en-1-yl Acetate (1) and Tetradec-11E-en-1-yl Acetate (2).** A mixture of 3 ml of THF, 20 ml of diglyme, and 0.7 ml of  $\text{LiAlH}_4$  was heated (Ar, bath temperature 160°C), and 3.5 ml of distillate was collected, after which the temperature was lowered to that of the room, and 1.2 g of the alcohol (11) or 1.42 g of the alcohol (12) was added dropwise. The reaction mixture was heated to 140°C (bath temperature) and was stirred for 36 h, after which it was cooled to room temperature, treated with 3.5 ml of water, neutralized with 10% HCl, and extracted with ether. The extract was washed with saturated NaCl solution, dried with  $\text{Na}_2\text{SO}_4$  and evaporated. To the residue from each experiment was added 6 ml of a mixture (2:3) of acetic anhydride and pyridine and the mixture was kept at room temperature (Ar, 24 h), and was then diluted with 100

ml of  $\text{CH}_2\text{Cl}_2$ , washed successively with 10% HCl, saturated solutions of  $\text{NaHCO}_3$  and NaCl, dried with  $\text{MgSO}_4$ , and evaporated. The residue was chromatographed ( $\text{SiO}_2$ , *n*-hexane–diethyl ether (10:1)) to give 1.1 g (85%) of the acetate (1),  $n_D^{20}$  1.4450 (see [22]) and 1.3 g (84%) of acetate (2),  $n_D^{20}$  1.4477 (see [6]). According to the results of capillary GLC, the amount of (Z)-isomer in each acetate was less than 1%. The IR, PMR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra were identical with those given in [5] and [22], respectively.

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