INSECT PHEROMONES AND THEIR ANALOGUES

XXXVI. SYNTHESIS OF 13-HYDROXY-2-OXOTRIDECANE – AN ATTACTANT OF THE HONEYBEE

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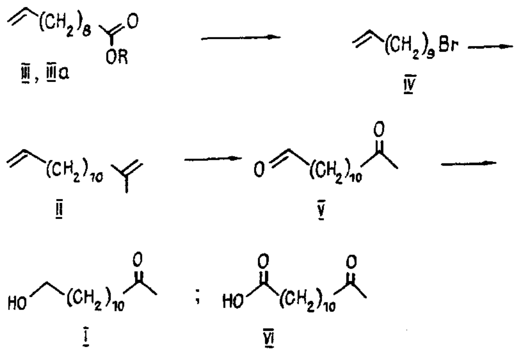
A six-stage synthesis of 13-hydroxy-2-oxotridecane – a sex attractant of the honeybee – has been achieved with the use of ozonoloysis as the key stage.

13-Hydroxy-2-oxotridecane (I), which has been isolated from an extract of the nectariferous plant Evodia hupehensis Dode, actively attracts honeybees [1]. No synthesis of this compound has been reported in the literature. We have developed a simple scheme for the synthesis of the attractant (I) the key stage of which was the ozonolysis of 2-methyltetradeca-1,13-diene (II). Diene (II) was obtained from undec-10-enoic acid (III, R = H), for which its methyl ester (IIIa, R = Me) was converted in two stages, as described in [2], into 1-bromoundec-10-ene (IV), which was coupled with methallyl chloride by the Grignard reaction catalyzed by cuprous iodide. Ozonolysis of the diene (II) followed by treatment of the ozonolysis product with dimethyl sulfide yielded 1,12-dioxotridecane (V).* Reduction of the ketoaldehyde with sodium triacetoxyhydroborate [3] took place selectively at the aldehyde group and led in good yield to the desired ketoalcohol (I)



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film). PMR spectra for compounds (I), (V), and (VI) were recorded on a Tesla BS-467 instrument (working frequency 60 MHz), and for compound (II) on a Tesla BS-567 instrument (100 MHz), with $CDCl_3$ or CCl_4 as solvent, the chemical shifts being given on the δ scale relative to the signal of TMS (internal standard). Mass spectra were measured on an MKh-1320 instrument at a temperature of the ionization chamber of 100°C and an ionizing energy of 70 eV. GLC analysis was conducted on a Chrom-5 instrument with the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at a working temperature of 50-300°C, the carrier gas being helium. The elementary analyses of the compounds synthesized corresponded to the calculated figures.

2-Methyltetradeca-1,13-diene (II). A mixture of 1.15 g ($6\cdot10^{-3}$ mole) of CuI and 0.98 g ($6\cdot10^{-3}$ mole) of 2,2'-bipyridyl in 20 ml of THF was treated (0°C, Ar) with 2.5 g ($27.6\cdot10^{-3}$ mole) of methallyl chloride and was stirred for 0.5 h, and then the Grignard reagent obtained

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*When the ketoaldehyde (V) was kept in the air for a week, it was wholly converted into the corresponding acid (VI).

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from 3.9 g ($17 \cdot 10^{-3}$ mole) of 1-bromoundec-10-ene (IV) [2] and 0.4 g ($17 \cdot 10^{-3}$ g-atom) of magnesium in 30 ml of absolute THF was added over 0.5 h; the reaction mixture was stirred at 0°C for 4 h and was then treated with 20 ml of saturated NH_4Cl solution and, after dilution with diethyl ether, it was washed successively with saturated solutions of NH_4Cl and of NaCl and was dried with $MgSO_4$ and evaporated. This gave 3 g (82%) of compound (II), n_D^{18} 1.4510.

IR spectrum (ν, cm^{-1}): 900 ($C{=}CH_2$), 925, 1010, 3090 ($CH{=}CH_2$), 1660 ($C{=}C$). PMR spectrum (100 MHz, $CDCl_3$): 1.15-1.40 (m, 16H, CH_2), 1.71 (C, 3H, CH_3-2), 2.0 (t, 4H, J = 7 Hz, H-3, H-12), 4.67 (s, 2H, H-1), 4.87-5.0 (m, 2H, H-14), 5.6-5.9 (m, 1H, H-13). Mass spectrum (m/z, %): 208(5.71), 166(1.26), 152(3.87), 124(5.91), 123(7.34), 110(14.28), 109(15.51), 97(11.83), 96(28.57), 95(26.12), 83(22.44), 68(24.48), 67(32.65), 57(40.81), 56(100.0), 55(75.51), 43(24.48), 41(69.38), 29(21.22).

1,12-Dioxotridecane (V) and 12-Oxotridecanoic Acid (VI). A mixture of ozone and oxygen (2 wt-% of O_3) was passed at the rate of 5 liters/h through a solution of 2.36 g ($11 \cdot 10^{-3}$ mole) of diene (II) in 30 ml of absolute ethyl acetate and 6 ml of abs. MeOH at 0°C until 1.06 g ($22 \cdot 10^{-3}$ mole) of ozone had been absorbed. Then the reaction mixture was purged with argon, 4 ml of Me_2S was added, and the mixture was stirred for 20 h and was evaporated. Diethyl ether was added to the residue, and the resulting solution was washed with water, dried with $MgSO_4$, and evaporated. The new residue was chromatographed [SiO_2, hexane—diethyl ether (1:1)]. This gave 1.44 g (60%) of the ketoaldehyde (V). IR spectrum (ν, cm^{-1}): 1715, 2730 ($C{=}O$). PMR spectrum (60 MHz, $CDCl_3$): 1.1-1.7 (m, 16 H, CH_2), 2.03 (s, 3H, H-13), 2.2-2.5 (m, 4H, H-2, H-11), 9.7 (m, 1H, H-1). After a week in the open air the ketoaldehyde (V) had been converted into 12-oxotridecanoic acid (VI), mp 67.0-67.5°C.

PMR spectrum (60 MHz, $CDCl_3$): 1.1-1.7 (m, 16H, CH_2), 2.0 (s, 3H, H-13), 2.15-2.5 (m, 4H, H-2, H-11), 10.7 (br. s, 1H, CO_2H). Mass spectrum (m/z, %): 228(50.87), 212(15.78), 210(10.52), 189(32.45), 182(70.10), 181(33.33), 170(33.33), 160(17.54), 152(84.21), 135(15.78), 125(14.03), 111(15.78), 98(19.29), 95(24.56), 85(29.82), 81(33.33), 73(42.98), 67(42.10), 58(43.85), 45(19.29), 43(100).

13-Hydroxy-2-oxotridecane (I). A solution of 0.78 g ($3.6 \cdot 10^{-3}$ mole) of the ketoaldehyde (V) in 10 ml of benzene was added dropwise to a suspension of sodium triacetoxyhydroborate obtained by the addition of 3.34 ml ($126 \cdot 10^{-3}$ mole) of AcOH to 1.37 g ($36 \cdot 10^{-3}$ mole) of $NaBH_4$ in 30 ml of benzene; the reaction mixture was stirred for 2.5 h and was decomposed with 20 ml of H_2O—ether (9:1). After evaporation in vacuum, the residue was treated with 300 ml of diethyl ether, and the resulting solution was decanted off and was washed successively with saturated solutions of $NaHCO_3$ and of NaCl and was dried with Na_2SO_4 and evaporated. This yielded 0.64 g (83%) of the hydroxyketone (I), mp 54.0-54.5°C [1]. IR spectrum (ν, cm^{-1}): 1080 ($C{-}O$), 1715 ($C{=}O$), 3200-3400 (OH). PMR spectrum (60 MHz, CCl_4): 1.1-1.5 (m, 18H, CH_2), 2.0 (s, 3H, H-13), 2.27 (t, 2H, J = 6 Hz, H-11), 3.5 (t, 2H, J = 6.5 Hz, H-1).

LITERATURE CITED

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