INSECT PHEROMONES AND THEIR ANALOGUES

XXV. SYNTHESIS OF ACETYLENIC PRECURSORS OF PHEROMONES FROM UNDECYLENIC ACID

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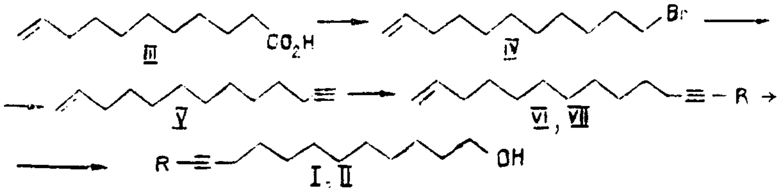
The selective ozonolysis of pentadec-1-en-12-yne and heptadec-1-en-12-yne, synthesized from the readily available undecylenic acid, has given tetradec- and hexadec-11-yn-1-ols — acetylenic precursors of a number of pheromones of insects of the order Lepidoptera.

The acetates of tetradec-11Z- and -11E-en-1-ols and of hexadec-11Z-en-1-ol, and also hexadec-11Z-enal, which are components of the pheromones of many species of insects of the order Lepidoptera [1], are produced from the acetylenic precursors tetradec- and hexadec-11-yn-1-ols [2-6].

From the readily available undecylenic acid (III), after its transformation according to [7] in the undecenyl bromide (IV), tridec-1-en-12-yne (V) was obtained with a yield of 83%. The interaction of the lithium derivative of the latter with ethyl and butyl bromides, just like the ethynylation of the bromoalkene (IV), took place most smoothly in a mixture of liquid ammonia, DMSO, and THF. The yields of coupling products — pentadec-1-en-12-yne (VI) and heptadec-1-en-12-yne (VII) — amounted to 79 and 85%, respectively. The ozonolysis of the enynes (VI and VII) took place exclusively at the vinyl group and, after the reduction of the peroxide products of ozonolysis with sodium tetrahydroborate in methanol, led to the desired alk-11-yn-1-ols (I and II). The overall yields of the acetylenic alcohols (I) and (II), calculated on the initial acid (III) amounted to 40 and 44%, respectively.



R = E(I, VI), N-Bu(II, XII)

EXPERIMENTAL

IR spectra were taken in a UR-20 spectrometer (in a film) and PMR spectra on a Tesla BS-567 spectrometer with a working frequency of 100 MHz using $CDCl_3$ as solvent. Chemical shifts are given in the δ scale relative to the signal of TMS (internal standard). Mass spectra were measured on a 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 using as the stationary phase the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at working temperatures of 50-300°C with helium as the carrier gas.

Tridec-1-en-12-yne (V). Acetylene (1 liter) was passed at the rate of 50 ml/min through a suspension of lithium amide obtained from 0.19 g (0.027 g-atom) of lithium, 0.02 g of ferric chloride, and 50 ml of liquid ammonia. Over 5 min, 4.23 g (0.18 mole) of the bromide (IV)

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(obtained from the acid (III) according to [7]; yield 73%, n_D^{20} 1.4516) in 5 ml of absolute THF was added to the resulting suspension of lithium acetylenide and, immediately afterwards, 5 ml of absolute DMSO was also added. The mixture was stirred at −35°C for 3 h, and stirring was continued until the ammonia had evaporated completely (3-4 h), after which 20 ml of water was added and the products were extracted with ether (3 × 100 ml). The extracts were washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated, and the residue was chromatographed (neutral Al_2O_3, hexane). This gave 2.66 g (83%) of the enyne (XII), n_D^{20} 1.4481, bp 72-75°C (8 mm) [8].

IR spectrum (ν, cm^{-1}): 925, 1010, 1660, 3090, ($CH{=}CH_2$), 2100, 3325 ($C{\equiv}CH$). PMR spectrum (100 MHz, $CDCl_3$): 1.1-1.6 (m 14H, H-4, H-5, H-6, H-7, H-8, H-9, H-10), 1.93 (t, 2H, J = 2.5 Hz, H-11), 1.8-2.16 (m, 3H, H-3, H-13), 4.8-5.1 (m, 2H, H-1) 5.55-5.98 (m, 1H, H-2). Mass spectrum, m/z (%): 164(0.60), 149(3.53), 135(11.34), 121(19.51), 107(20.73), 93(43.90), 81 (59.75), 79(64.63), 68(41.46), 67(82.92), 55(100.00), 54(31.70), 53(21.95), 43(21.95), 41(56.09), 29(19.51), 27(14.63).

Pentadec-1-en-12-yne (VI). A solution of 1.78 g (0.01 mmole) of the enyne (V) in 10 ml of absolute THF was added to a suspension of lithium amide obtained from 0.14 g (0.02 (g-atom) of lithium, 0.02 g of ferric chloride, and 100 ml of liquid ammonia, the mixture was stirred for 40 min, and then 2.18 g (0.02 mole) of ethyl bromide and, immediately after it, 10 ml of absolute DMSO were added. The resulting mixture was stirred at -35°C for 4 h and then for another 4 h (until the ammonia had evaporated completely), 20 ml of water was added, and the products were extracted with hexane (3 × 100 ml). The extracts were washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated, and the residue was chromatographed (SiO_2, hexane). This gave 1.63 g (79%) of the enyne (VI), n_D^{20} 1.4564.

IR spectrum (ν, cm^{-1}): 915, 990, 1645, 3070 ($CH{=}CH_2$), 2350 ($C{\equiv}C$). PMR spectrum (100 MHz, $CDCl_3$): 1.11 (t, 3H, J = 7.5 Hz, H-15), 1.18-1.45 (m, 14H, H-4, H-5, H-6, H-7, H-8, H-9, H-10), 1.85-2.22 (m, 6H, H-3, H-11, H-14), 4.8-5.06 (m, 2H, H-1), 5.57-5.96 (m, 1H, H-2). Mass spectrum, m/z (%): 206(0.50), 191(1.84), 177(12.63), 163(5.53), 149(15.00), 138(1.32), 135(15.53), 121(19.74), 109(40.79), 107(23.68), 95(65.79), 93(27.63), 81(72.37), 79(32.89), 68(44.74), 67(100.00), 55(65.79),43(18.42), 41(71.05).

Heptadec-1-en-12-yne (VII). A solution of 1.78 g (0.01 mole) of the enyne (V) in 10 ml of absolute THF was added to a suspension of lithium amide obtained from 0.14 g (0.02 g-atom) of lithium, 0.02 g of ferric chloride, and 100 ml of liquid ammonia, the mixture was stirred for 40 min, and then 2.74 g (0.02 mole) of butyl bromide and, immediately after it, 10 ml of absolute DMSO were added. A working-up procedure similar to that given above for compound (VI) yielded 2.0 g (85%) of the enyne (VII), n_D^{20}1.4568. The IR, PMR, and mass spectra were identical with those described in the literature [3].

Tetradec-11-yn-1-ol (I). A mixture of ozone and oxygen (2 wt. -% of O_3) was passed at the rate of 5 liters/h through a solution of 0.31 g (0.0015 mole) of the enyne (VI) in 5 ml of cyclohexane containing 0.15 ml of absolute methanol until 1.5 mmole of ozone had been absorbed. The reaction mixture was purged with argon, and, after the addition of 2 ml of methanol and 0.09 g (0.0024 mole) of sodium tetrahydroborate at 10°C, it was stirred at room temperature for 15 h, and then 1 ml of a 10:1 mixture of water and acetic acid was added, stirring was continued at 20°C for 1 h, and the resulting mixture was evaporated under reduced pressure. The residue was dissolved in 100 ml of diethyl ether, and the solution was washed with saturated $NaHCO_3$ solution, dried with Na_2SO_4, and evaporated. Chromatography of the residue (SiO_2, hexane—diethyl ether 7:3) gave 0.26 g (83%) of the alkynol (I), n_D^{20} 1.4645. Its IR and PMR spectra were identical with those given in the literature [2].

Hexadec-11-yn-1-ol (II). The ozonolysis of 0.35 g (0.0015 mole) of the enyne (VII), as described in the preceding experiment, yielded 3 g (85%) of the alkynol (II), n_D^{20} 1.4657. Its IR and PMR spectra were identical with those given in the literature [2].

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