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INSECT PHEROMONES AND THEIR ANALOGUES

XLIV. CHIRAL PHEROMONES BASED ON (S)-(+)-3,7-DIMETHYLOCTA-1,6-DIENE

4. SYNTHESIS OF (S)-14-METHYLOCTADEC-1-ENE — SEX PHEROMONE OF Lyonetia clerkella

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UDC 547.381+542.91+632.936.2

The synthesis has been achieved of optically active (S)-(+)-14-methyloctadec-1-ene — the sex pheromone of the leaf miner peach moth Lyonetia clerkella Linne from the readily accessible enantiomerically enriched (ee ≈ 50%) (S)-(+)-3,7-dimethyloct-1,6-diene.

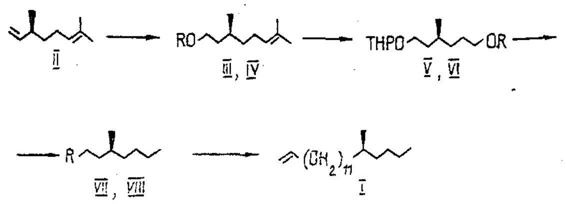
Syntheses of (S)-14-methyloctadec-1-ene (I) — the sex pheromone of the leaf miner peach moth (Lyonetia clerkella L.) — are known that start from (R)-(+)-pulegone [1] and from methyl (R)-3-hydroxy-2-methylpropionate [2]. A synthesis based on the product of the epoxidation of the trisubstituted double bond in a readily accessible chiral compound (ee ≈ 50%) — (S)-3,7-dimethylocta-1,6-diene (dihydromyrcene) (II) has also been published [3].

We propose a new pathway for the conversion of the diene (II) into the desired pheromone (I). By using the hydroalumination reaction, diene (II) was smoothly converted into β-(−)-citronellol (III) [4]. Ozonolysis of the tetrahydropyranyl ether (IV) of the alcohol (III) in methanol, followed by the sodium tetrahydroborate reduction of the peroxidic ozonolysis product, gave (S)-6-(tetrahydropyan-2-yloxy)-4-methylhexan-1-ol (V), which was converted into the corresponding tosylate (VI). The Li_2CuCl_4-catalyzed methylation of the tosylate (VI) with the aid of methylmagnesium iodide gave (S)-3-methylheptan-1-ol (VII). Bromination of the alcohol (VII) with phosphorus tribromide, followed by the coupling of the resulting bromide (VII) with undecenylmagnesium bromide in the presence of CuI and 2,2'-bipyridyl led to the desired pheromone (I), the overall yield of which, calculated on the initial dihydromyrcene (II), amounted to 17.1%.

From a comparison of the specific angle of rotation found for alkene (I) ($[\alpha]_D^{20}$ + 0.59°) with literature figures [1] for an optically pure specimen ($[\alpha]_D^{20}$ + 1.20°), it followed that the optical purity of the pheromone obtained was ≈50%, which corresponded to the optical purity of the initial dihydromyrcene [5].

Institute of Organic Chemistry, Urals Branch, Russian Academy of Sciences, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 714-717, November-December, 1992. Original article submitted December 18, 1991.

0009-3130/92/2806-0621$12.50



R = H(III, V), THP(IV), Ts(VI), OH(VII), Br(VIII)

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film), and PMR spectra were recorded on a Tesla BS-67 instrument (working frequency 60 MHz, solvent CCl_4), the chemical shifts being given on the δ scale relative to HMDS (internal standard). GLC analysis was conducted on a Chrom-41 instrument with the stationary phase Carbowax-6000 (5%) on the support Inerton Super (0.125-0.160 mm) at a working temperature of 50-170°C, the carrier gas being helium. $[\alpha]_D$ values were determined for solutions in $CHCl_3$ on a Perkin–Elmer-141 polarimeter. The analytical results for the compounds synthesized corresponded to the calculated figures.

(3S)-3,7-Dimethyl-1-(tetrahydropyran-2-yloxy)oct-6-ene (IV). A solution of 9.49 g ($60.6 \cdot 10^{-3}$ mole) of (3S)-3,7-dimethyloct-6-en-1-ol, obtained from (S)-3,7-dimethyloct-1,6-diene (II) according to [4], and 0.12 g of TsOH in 175 ml of abs. diethyl ether was treated at 10-15°C with 21.9 g (0.26 mole) of 2,3-dihydro-4H-pyran, and the mixture was heated to room temperature and stirred for 20 h, after which 200 ml of diethyl ether was added, and it was washed successively with saturated solutions of $NaHCO_3$ and of NaCl, and was dried with Na_2SO_4 and evaporated. This gave 12.56 g (86%) of compound (IV). IR spectrum (ν, cm^{-1}) 1050, 1090, 1135, 1150, 1195 (C–O, O–C–O); 835, 1655 (C=C).

(S)-6-(Tetrahydropyran-2-yloxy)-4-methylhexan-1-ol (V). A mixture of ozone and oxygen ($15 \cdot 10^{-3}$ mole of O_3/h) was bubbled through a solution of 12.5 g ($52 \cdot 10^{-3}$ mole) of compound (IV) in 80 ml of abs. methanol at 5°C until 2.5 g ($52 \cdot 10^{-3}$ mole) of ozone had been absorbed. The reaction mixture was purged with argon, and then 3.35 g ($39 \cdot 10^{-3}$ mole) of $NaBH_4$ was added while the temperature was maintained at 15-20°C. The resulting mixture was stirred for 12 h, diluted with 1 liter of diethyl ether, washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. This gave 9.58 g (85%) of the hydroxyether (V), n_D^{20} 1.4629, $[\alpha]_D^{23}$-0.31° (c 7.4; $CHCl_3$). IR spectrum (ν, cm^{-1}): 1050, 1080, 1135, 1150, 1195, (C–O, O–C–O), 3200-3600 (O–H). PMR spectrum (60 MHz, CCl_4): 0.85 (d, 3H, J = 5.5 Hz, CH_3-4), 1.17-2.17 (m, 13 H, H-2–5, H-3'–5'), 2.67 (br. s, 1H, OH), 3.12-4.12 (m, 6H, H-1.66'), 4.43 (br. s, 1H, H-2').

(S)-3-Methyl-1-(tetrahydropyran-2-yloxy)-6-tosyloxyhexane (VI). At 0°C, 9.56 g ($44.3 \cdot 10^{-3}$ mole) of the alcohol (V) was added to a solution of 10.11 g ($53 \cdot 10^{-3}$ mole) of TsCl in 34 ml of pyridine, and the reaction mixture was left overnight in the refrigerator and was then poured onto ice (70 g) and extracted with diethyl ether (3 × 150 ml). The extract was washed successively with saturated solutions of $CuSO_4$, $NaHCO_3$, and NaCl, and was dried with Na_2SO_4, and evaporated. This gave 15.39 g (94%) of the tosylate (VI). IR spectrum (ν, cm^{-1}): 1030, 1075, 1110, 1195 (C–O, O–C–O); 1185, 1370 (S=O); 1600 (Ar).

(S)-3-Methylheptan-1-ol (VII). With stirring (–45°C, Ar), a solution of 6.90 g ($21.8 \cdot 10^{-3}$ mole) of the tosylate (VI) in 100 ml of abs. THF was added dropwise to the Grignard reagent obtained from 5.76 g (0.24 gram-atom) of Mg and 30.96 g (0.218 mole) of methyl iodide in 22 ml of abs. diethyl ether, after which, at –67°C, 10.9 ml of a 0.1 M solution of Li_2CuCl_4 in THF was added, the reaction mixture was stirred for 1.5 h, and then the temperature was brought to that of the room during 1 h, and it was left overnight. Then the reaction mixture was diluted with 100 ml of diethyl ether and was poured into a cold saturated solution of NH_4Cl. The organic layer was separated off, and the aqueous layer was extracted with diethyl ether (3 × 100 ml). The combined extract and organic layer were washed successively with saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl, and were evaporated. The residue was chromatographed (SiO_2, hexane–diethyl ether (7:3)), giving 1.65 g (64%) of the alcohol (VII), with a purity, according to GLC analysis, ≥96% R_f 0.28, n_D^{24} 1.4255, $[\alpha]_D^{24}$-1.08° (c 3.01; $CHCl_3$) (see [6]). IR spectrum (ν, cm^{-1}): 1055 (C–O), 1385, 1475 (CH_3–C), 3350 (O–H). PMR spectrum (60 MHz, CCl_4): 0.67-1.00 (m, 6H, CH_3-3, H-7), 1.07-1.67 (m, 9H, H-2–6), 3.13 (br. s, 1H, OH), 3.51 (t, 2H, J = 7 Hz, H-1).

(S)-1-Bromo-3-methylheptane (VIII). With stirring (−10°C, Ar), 0.90 g ($3.32 \cdot 10^{-3}$ mole) of PBr_3 was added to a solution of 0.97 g ($7.46 \cdot 10^{-3}$ mole) of the alcohol (VII) and 0.18 g of ($2.63 \cdot 10^{-3}$ mole) of pyridine in 8 ml of abs. diethyl ether, and the resulting mixture was stirred at room temperature for 2 days. Then it was cooled to 0°C and, after the addition of a saturated solution of NH_4Cl, it was extracted with diethyl ether (3 × 150 ml). The extract was washed successively with saturated solutions of NH_4Cl and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, pentane), to give 1.27 g (88%) of the bromide (VIII), n_D^{21} 1.4513, $[\alpha]_D^{27}$ + 3.71° (c 3.27; $CHCl_3$). Its IR and PMR spectra were identical with those given in the literature [7].

(S)-14-Methyloctadec-1-ene (I). To a stirred suspension of 0.27 g ($1.12 \cdot 10^{-3}$ mole) of CuI in 11 ml of abs. THF was added 0.18 g ($1.21 \cdot 10^{-3}$ mole) of 2.2'-bipyridyl, and the mixture was stirred for 0.5 h (20°C, Ar) and was then cooled to 2°C, and a solution of 1.08 g ($5.6 \cdot 10^{-3}$ mole) of the bromide (VIII) in 11 ml of abs. THF was added. The resulting mixture was stirred for 0.5 h and was treated with a solution of the Grignard reagent obtained from 0.25 g ($10.4 \cdot 10^{-3}$ g-atom) of Mg and 1.96 g ($8.4 \cdot 10^{-3}$ mole) of undec-10-enyl bromide in 20 ml of abs. THF, and the reaction mixture was stirred at 2°C for 2 h and at room temperature for 16 h, and, after the addition of 25 ml of saturated NH_4Cl solution, at 10°C for a further 1 h. It was then extracted with diethyl ether (3 × 150 ml), and the extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2; hexane) and redistilled. This gave 0.84 g (71%) of the alkene (I), bp 119-128°C (0.5 mm), $[\alpha]_D^{23}$ + 0.59° (c 3.0, $CHCl_3$). Its IR and PMR spectra were identical with those given in the literature [3].

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