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INSECT PHEROMONES AND THEIR ANALOGUES

XLII. SYNTHESIS OF 2,6-DIMETHYLOCT-1-YL FORMATE – A MIMIC OF THE AGGREGATION PHEROMONE OF FLOUR BEETLES

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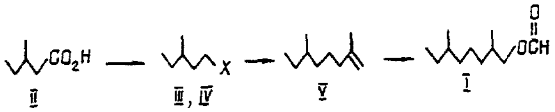
UDC 547.381+542.91+632.936.2

2-6-Dimethyloctan-1-ol, the formate of which is a mimic of the aggregation pheromone of the flour beetles Tribolium confusum and T. castaneum, has been synthesized by the hydroboration of 2,6-diemthyloct-1-ene, obtained from β-methylvaleric acid.

The aggregation pheromone of the flour beetles Tribolium confusum and T. castaneum, which has been identified as 4,8-dimethyldecanal [1], is deactivated under the conditions of use, being oxidized in the air. A stable analogue of the pheromone has been found – 2,6-dimethyloct-1-yl formate (I) – for which a five-stage synthesis based on the condensation of methyl sodiomalonate with the difficultly accessible 4-methylhex-3E-en-1-yl bromide has been proposed [2].

We have developed a more rational route for the synthesis of the formate (I) from the available β-methylvaleric acid (II). Its reductioin to 3-methylpentan-1-ol with the aid of lithium tetrahydroaluminate took place with a high yield, as also did the following oeprations for obtaining the bromide (IV), which are described in [3]. Condensation of the bromide (IV) with methallyl chloride completed the construction of the carbon skeleton, and hydroboration of 2,6-dimethyloct-1-ene (V) so obtained, with oxidation of the organoboron intermediate by alkaline H_2O_2 and treatment with formic acid, led to the desired formate (I), the overall yield of which amounted to 54%, calculated on the initial acid (II).



X=OH(III), Br(IV)

Institute of Organic Chemistry, Urals Branch, Russian Academy of Sciences, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 571-573, September-October, 1992. Original article submitted October 28, 1991.

EXPERIMENTAL

IR spectra were taken on 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, the chemical shifts being given in the δ scale relative to the signal of TMS (internal standard). GLC analysis was conducted on a Chrom-5 instrument, with silicone SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) as the stationary phase at a working temperature of 50-300°C using helium as the carrier gas.

2-Methylpental-1-ol (III). At 20°C, under argon, a solution of 9.5 g ($82.0 \cdot 10^{-3}$ mole) of 3-methylpentanoic acid (II) in 37 ml of abs. diethyl ether was added to a suspension of 3.23 g ($8.50 \cdot 10^{-3}$ mole) of $LiAlH_4$ in 50 ml of abs. diethyl ether; the mixture was boiled for 2 h and was then cooled to 0°C, treated dropwise with 7 ml of water, and stirred for 1 h at room temperature, after which it was extracted with diethyl ether (4 × 100 ml), and the extract was dried with $NaSO_4$ and distilled. This gave 7.86 g (94%) of the alcohol (III), n_D^{25} 1.4112, b.p. 152°C, IR and PMR spectra identical with those given in [3].

2,6-Dimethyloct-1-ene (V). At −15°C, under argon, 1.6 ml of a 0.1 M solution ($0.16 \cdot 10^{-3}$ mole) of Li_2CuCl_4 was added to a solution of 3.0 g ($33.0 \cdot 10^{-3}$ mole) of methallyl chloide in 14 ml of abs. THF; the mixture was stirred for 10 min, and then a solution of the Grignard reagent prepared in 90 ml of abs. THF from 1.24 g ($51.0 \cdot 10^{-3}$ g-atom) of magnesium and 8.11 g ($49.0 \cdot 10^{-3}$ mole) of 1-bromo-3-methylpentane (IV), obtained from the alcohol (III) with a yield of 79% according to [3], was added dropwise. The reaction mixture was stirred at −10°C for 2 h and its temperature was then raised to that of the room over 1 h, and, after another 12 h, 50 ml of a saturated solution of NH_4Cl cooled to 5°C was added, the products were extracted with diethyl ether (3 × 200 ml), and the extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was distilled, to give 6.12 g (89%) of the olefin (V), bp 70-71°C (35 mm), IR and PMR spectra identical with those given in [4].

2,6-Dimethyloct-1-yl Formate (I). At 25°C, under argon, a solution of 2.9 ml of $BF_3 \cdot Et_2O$ in 11 ml of abs. THF was added dropwise to a suspension of 4.86 g ($33.0 \cdot 10^{-3}$ mole) of the alkene (V) and 0.73 g ($19.3 \cdot 10^{-3}$ mole) of $NaBH_4$, and, after stirring for 2 h, 1.5 ml of water and then 30 ml of a mixture (1:1) of a 3 N solution of NaOH and 30% H_2O_2 was added, and the reaction mixture was stirred for 15 h; then it was extracted with diethyl ether (3 × 200 ml), and the extract was washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. The residue (4.86 g) after chromatography [SiO_2, hexane–diethyl ether (7:3)] was dissolved in a mixture of 25.5 ml of HCOOH and 12 ml of abs. THF, and the solution was stirred at room temperature for 2 h and it was then diluted with diethyl ether (0.5 liter) and was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, pentane–diethyl ether (9:1)], giving 5.08 g (82%) of the formate (I), n_D^{26} 1.4269 [2]. IR spectrum (ν, cm^{-1}): 1195 (C–O–C), 1385 (CH_3), 1730 (C=O). PMR spectrum (100 MHz, $CDCl_3$): 0.7-1.0 (m, 9H, CH_3), 1.05-1.85 (m, 8H, CH_2, CH), 3.88-4.1 (m, 2H, H-1), 8.08 (s, 1H, $\underset{\underset{O}{\|}}{HC}{-}O$).

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