studied. It has been shown that spatial screening by the neighboring methyl substituent of the amino group in  $N_1$ -methylguanosine leads to its complete deactivation in acylation, tetrahydropyranylation, and tritylation reactions.

2. N,O-Protected 2'-O-methyl and 2'-O-tetrahydropyranyl derivatives of cytidine, guanosine, and  $N_1$ -methylguanosine have been synthesized.

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## INSECT PHEROMONES AND THEIR ANALOGUES.

XXII. METHYL-BRANCHED PHEROMONES BASED ON

4-METHYLTETRAHYDROPYRAN.

SYNTHESIS OF RACEMIC 2-ACETOXY-3,7-DIMETHYLPENTADECANE (DIPRIONYL ACETATE)

UDC 547.3+632.78

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A synthesis is proposed of racemic 2-acetoxy-3,7-dimethylpentadecane - the sex attractant (diprionyl acetate) of plane sawflies of the genera <u>Diprion</u> and <u>Neo-</u><u>diprion</u> on the basis of the regioselective transformation of bifunctional products of the cleavage of 4-methyltetrahydropyran.

Syntheses are given in the literature both of racemates [1-7] and of optically active forms [8-12] of 2-acetoxy-3,7-dimethylpentadecane (I) - the sex pheromone of plane sawflies of the genera <u>Diprion</u> and <u>Neodiprion</u>. Since racemic (I), known under the name of diprionyl acetate, exhibits biological activity [1] it is economically desirable to use just this as the attractant.

We have developed a practical synthesis of the racemic acetate (I) based on the regioselective transformations of the methyl-branched bromohydrin (III) obtained by the cleavage of the readily available 4-methyltetrahydropyran (II) [13]. The coupling of compound (III)

Institute of Chemistry, Bashkir Scientific Center, Urals Branch, USSR Academy of Sciences. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 573-576, July-August, 1989. Original article submitted October 17, 1988; revision submitted January 9, 1989. with n-hexylmagnesium bromide under the action of Kochi's catalyst [14] followed by acid hydrolysis gave 3-methyldecan-1-ol (IV), which was converted into the corresponding bromide (V). The transformation of the latter into the Grignard reagent and condensation with methallyl chloride led to 2,6-dimethyltetradec-1-ene (VI). The hydroboration of the double bond in the olefin (VI) took place regioselectively and, after the oxidation of the organoboron intermediate, led to 2,6-dimethyltetradecan-1-ol (VII), the oxidation of which gave the corresponding aldehyde (VIII). Coupling the latter with methylmagnesium iodide as described in [4] gave the desired acetate (I). The yield of diprionyl acetate (I) calculated on the bromohydrin (III) was 25%.



# X = OH(IV), Br(V)

#### EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film), and PMR spectra were recorded on a Tesla BS-467 instrument (working frequency 60 MHz) with CCl<sub>4</sub> as solvent and HMDS as internal standard. GLC analysis was performed on a Chrom-5 instrument with the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) as the mobile phase at working temperatures of 50-300°C using helium as the carrier gas. The mass spectrum of compound (I) was measured on a MKh-1306 instrument at a temperature of the ionization chamber of 150°C and at an ionizing energy of 70 eV.

<u>3-Methylundecan-1-ol (IV)</u>. A solution of 5.0 g (0.0189 mole) of the bromohydrin (III) in 3 ml of absolute THF (Ar) at -10°C was treated successively with 9.4 ml of a 0.1 M solution of Li<sub>2</sub>CuCl<sub>4</sub> in absolute THF and with a solution of the Grignard reagent obtained from 0.98 g (0.0408 g-atom) of magnesium and 6.24 g (0.0378 mole) of n-hexyl bromide in 40 ml of absolute THF, and the mixture was stirred at the same temperature for 1 h and then at 5°C for 2 h and at room temperature for 15 h, after which it was cooled to 5°C and 30 ml of 10% HCl was added to it; the resulting mixture was warmed to room temperature, stirred for 0.5 h, and extracted with diethyl ether (3 × 170 ml). The extract was evaporated, the residue was dissolved in 43 ml of methanol, this solution was treated with 8 ml of water and 0.43 g of TsOH, and the mixture was boiled for 3 h, after which it was evaporated and the residue was extracted with diethyl ether (2 × 250 ml). The extract was washed with saturated NaHCO<sub>3</sub> solution, dried with Na<sub>2</sub>SO<sub>4</sub>, and evaporated, and the residue was chromatographed (SiO<sub>2</sub>, hexane-diethyl ether (7:3)). This gave 2.67 g (76%) of the alcohol (IV),  $n_D^{25}$  1.4413 [12]. The IR and PMR spectra were identical with those described in [12].

<u>1-Bromo-3-methylundecane (V).</u> A mixture of 2.46 g (0.0132 mole) of the alcohol (IV), 3.0 ml of 48% HBr, and 0.78 ml of concentrated  $H_2SO_4$  was boiled for 6 h, and it was then cooled to room temperature, diluted with 10 ml of water, and extracted with hexane (3 × 100 ml); the extract was washed successively with saturated NaHCO<sub>3</sub> and NaCl solutions and was dried with MgSO<sub>4</sub> and evaporated. The residue was chromatographed (SiO<sub>2</sub>, hexane), giving 2.45 g (74.5%) of the bromide (V),  $n_D^{5}$  1.4579 [12]. The IR and PMR spectra were identical with those described in [12].

<u>2,6-Dimethyltetradec-1-ene (VI)</u>. A stirred suspension of 0.34 g of CuI in 20 ml of absolute THF was treated with 0.29 g of bi-2-pyridyl and the mixture was stirred for 0.5 h (20°C, Ar) and was then cooled to 2°C and a solution of 1.70 g (0.0188 mole) of methallyl chloride in 20 ml of absolute THF was added; the resulting mixture was stirred for 10 min, a solution of the Grignard reagent obtained from 0.34 g (0.0141 g-atom) of magnesium and 2.36 g (0.00948 mole) of the bromide (V) in 20 ml of absolute THF was added, and the reaction mixture was stirred at 2°C for 2 h and then at room temperature for 16 h. After this,

30 ml of saturated NH4Cl solution was added, the mixture was stirred at 10°C for 1 h and was extracted with diethyl ether  $(3 \times 200 \text{ ml})$ , and the extract was washed with saturated NaCl solution, dried with MgSO4, and evaporated. The residue was chromatographed (SiO2, hexane), giving 1.90 g (89.5%) of the olefin (VI). IR spectrum (v, cm<sup>-1</sup>): 890 (C-H); 1380, 1470 (CH<sub>3</sub>); 1650 (C=C); 3080 (C-H). PMR spectrum (60 MHz, CC1<sub>4</sub>): 0.75-0.95 (m, 6H, H-14, CH<sub>3</sub>-6), 1.18 (br.s, 19H, CH<sub>2</sub>, CH), 1.60 (s, 3H, CH<sub>3</sub>-2), 1.72-2.05 (m, 2H, H-3), 4.55 (s, 2H, H-1). Found, %: C 85.59; H 14.36. C16H32. Calculated, %: C 85.63; H 14.37. M 224.4.

2,6-Dimethyltetradecan-l-ol (VII). A solution of 0.84 ml of boron trifluoride etherate in 18 ml of absolute THF was added dropwise (20°C, Ar) to a suspension of 1.9 g (0.0085 mole) of the olefin (VI) and 0.19 g of sodium tetrahydroborate in 48 ml of absolute THF, the mixture was stirred for 3.5 h and then 1.7 ml of water and, after 10 min, 1.8 ml of a 3 N solution of NaOH and 1.8 ml of 30% H<sub>2</sub>O<sub>2</sub> were added and the reaction mixture was stirred and left for 16 h; after this, 350 ml of diethyl ether was added and the mixture was washed with saturated NaCl solution, dried with Na2SO4, and evaporated. The residue consisted of 1.70 g (83%) of the alcohol (VII),  $n_D^2$  1.4559 [15]. IR spectrum (v, cm<sup>-1</sup>): 1045 (C-O), 1375, 1465, 3200-3600 (OH).

2,6-Dimethyltetradecanal (VIII). With stirring, a solution of 0.9 g (0.0037 mole) of the alcohol (VII) in 2 ml of CH<sub>2</sub>Cl<sub>2</sub> was added to a suspension of 1.19 g of pyridinium chlorochromate in 14 ml of redistilled CH<sub>2</sub>Cl<sub>2</sub> (20°C, Ar). The reaction mixture was stirred at room temperature for 2 h and was then diluted with 100 ml of diethyl ether and filtered through a layer of SiO2, and, after the residue on the filter had been washed with 100 ml of diethyl ether, the solution was dried with  $MgSO_4$  and evaporated. This gave 0.66 g (74%) of the aldehyde (VIII), the IR and PMR spectra of which were identical with those given in [4].

2-Acetoxy-3,7-dimethylpentadecane (I). At 0°C under Ar, 0.36 g (0.0015 mole) of the aldehyde (VIII) in 1.5 ml of absolute diethyl ether was added to a solution of the Grignard reagent prepared from 0.36 g (0.0025 mole) of methyl iodide and 0.09 g (0.0038 g-atom) of magnesium in 3 ml of absolute diethyl ether, and the reaction mixture was stirred at the same temperature for 20 min, after which a solution of 0.5 g (0.005 mole) of acetic anhydride in 0.5 ml of absolute diethyl ether was added dropwise and the mixture was stirred at room temperature for 20 min; then 5 ml of a saturated solution of NH<sub>4</sub>Cl was added and, after being stirred for another 0.5 h, the mixture was extracted with diethyl ether  $(3 \times 50 \text{ ml})$ , and the extract was washed with saturated NaCl solution, dried with MgSO4, and evaporated. The residue was chromatographed (SiO<sub>2</sub>, hexane-diethyl ether (9:1)), giving 0.36 g (80%) of the acetate (I), the IR, PMR, and mass spectra of which were identical with those described in [4].

#### SUMMARY

Racemic 2-acetoxy-3,7-dimethylpentadecane - the sex attractant (diprionyl acetate) of plane sawflies of the genera Diprion and Neodiprion - has been synthesized from a bifunctional product of the cleavage of 4-methyltetrahydropyran.

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