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INSECT PHEROMONES AND THEIR ANALOGS.
LVII. SYNTHESIS OF THE RACEMIC ANALOG OF THE SEX PHEROMONE OF PINE SAWFLIES OF THE GENERA *Diprion* AND *Neodiprion*

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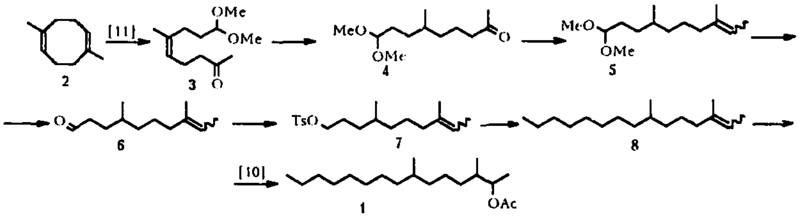
A new route has been developed to the selective transformations of *1,1-dimethoxy-4-methyl-8-oxonon-4Z-ene — a product of the partial ozonolysis of 1,5-dimethylcycloocta-1Z,5Z-diene — leading to (±)-3,7-dimethylpentadec-2-yl acetate, the racemic analog of the sex pheromone of pine sawflies of the* Diprion *and* Neodiprion *genera.*

Racemic (±)-3,7-dimethylpentadec-2-yl acetate (prionyl acetate) (**1**) exhibits the activity of the sex pheromone of four species of pine sawflies of the genera *Diprion* and *Neodiprion* [1, 2]. Several syntheses of the attractant (**1**) are known [2-9]. We have also reported the synthesis of compound (**1**) by selective transformations of 4-methyl-1,8-dioxonon-4Z-ene, including its selective reduction to a corresponding hydroxyketone and the protection of a keto group that is necessary in this case [10].

In the present communication we propose a shorter route to the synthesis of prionyl acetate (**1**) from 1,5-dimethylcycloocta-1Z,5Z-diene (**2**), the ozonolytic cleavage of which by a method described previously [11] leads to 1,1-dimethoxy-4-methyl-8-oxonon-4Z-ene (**3**). The use of the monoacetal (**3**) permitted a decrease in the number of stages and a doubling of the overall yield of the desired compound (**1**), which amounted to 20%, calculated on the initial isoprene dimer (**2**).



As the key stage in the proposed scheme of synthesis of the pheromone (**1**) we used the olefination of the saturated equivalent of the monoacetal (**3**) — 1,1-dimethoxy-4-methyl-8-oxononane (**4**), which is readily obtained by the catalytic hydrogenation of compound (**3**). Olefination of ketone (**4**) with ethylidenetriphenylphosphorane gave 1,1-dimethoxy-4,8-dimethyldec-8-ene (**5**) in the form of a mixture (~4:1) of the Z- and E-isomers, as followed from a GLC analysis in a capillary column and from the ratio of the intensities of the singlets of the protons of the vinyl methyl group, CH_3-8, resonating in the regions of δ 1.67 ppm (for the Z-isomer) and 1.54 ppm (for the E-isomer) [12]. Acid hydrolysis of the acetal (**5**) and reduction of the resulting 4,8-dimethyldec-8Z/E-enal (**6**) with a complex hydride ($NaBH_4$) led to the alcohol corresponding to aldehyde (**6**), which was converted into the tosylate — 1-tosyloxy-4,8-dimethyldec-8Z/E-ene (**7**). The Li_2CuCl_4-catalyzed coupling of the latter with amylmagnesium bromide took place smoothly, with the formation of 3,7-dimethylpentadec-2E/Z-ene (**8**) the hydroxylation of which under conditions found earlier [10] led to 3,7-dimethylpentadecan-2-ol, which was acetylated to the desired compound (**1**).

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EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer in a thin layer. PMR spectra were obtained on a Tesla BS-567 spectrometer (working frequency 100 MHz) with $CDCl_3$ as solvent and TMS as internal standard. GLC was conducted on a Chrom-5 instrument with the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm), flame-ionization detector, working temperature 50-300°C, carrier gas helium. In addition, compound (5) was analyzed on a Carlo Erba instrument with a glass capillary column (25 × 0.2 mm [sic]), working temperature 50-200°C. The elementary analysis of the compounds synthesized corresponded to the calculated values.

1,1-Dimethoxy-4-methyl-8-oxononene (4). A solution of 10.7 g (0.05 mole) of the monoacetate (3) in 600 ml of absolute ethanol–hexane (1:1) was hydrogenated (catalyst 5% Pd/C, ~25°C, normal pressure, 5 days) and, after filtration, the solution was passed through a 2.5-cm layer of SiO_2 and evaporated. This gave 10.5 g (97%) of compound (4), bp 108-110°C (2 mm), n_D^{20} 1.4383. The IR and PMR spectra were identical with those given earlier [13].

1,1-Dimethoxy-4,8-dimethyldec-8Z/E-ene (5). To a suspension of 8.5 g (0.023 mole) of ethylidenetriphenylphosphorane in 70 ml of absolute THF being stirred at −30°C under argon was added 17.6 ml of a 1.3 N solution of BuLi in hexane, and the mixture was stirred at −30°C for 0.5 h and was treated with a solution of 3.2 g (0.015 mole) of the ketoacetal (4) in 10 ml of THF. The reaction mixture was stirred at −30°C for 1 h and at 25°C for 15 h and was then diluted with 300 ml of hexane and filtered. The filtrate was washed with saturated aqueous NaCl, dried with $MgSO_4$, and evaporated in vacuum, and the residue was chromatographed on 100 g of Al_2O_3 (act. grade II). Elution with hexane–ether (3:1) gave 0.32 g of the initial substance (4) and 2.8 g (84%) of compound (5).

IR spectrum (ν, cm^{-1}): 860 (C=C–H), 1065 (C–O), 1380 (CH_3), 1670 (C=C).

PMR spectrum (δ, ppm): 0.8 (M, 3H, CH_3-4), 1.26 (m, 8H, CH_2), 1.54 s, 1.57 d, 1.65 d, and 1.67 s, (6H, $CH_3-C=C$), 1.7 (m, 1H, H-4), 2.07 (m, 2H, H-7), 3.32 (s, 6H, OCH_3), 4.33 (t, 1H, J = 5 Hz, H-1), 5.2 (m, 1H, H-9).

4,8-Dimethyldec-8Z/E-enal (6). A solution of 2.5 g (0.011 mole) of the acetal (5), 3 ml of H_2O, and 0.8 g of pyridinium tosylate in 130 ml of acetone was boiled for 2.5 h and was then evaporated in vacuum and the residue was dissolved in 500 ml of diethyl ether. The solution was washed successively with saturated aqueous solutions of NH_4Cl, Na_2CO_3, and NaCl, dried with $MgSO_4$, and evaporated in vacuum. This gave 2.0 g (98%) of the aldehyde (6). IR spectrum (ν, cm^{-1}): 860 (C=C–H), 1380 (CH_3), 1670 (C=C), 1720 (C=O), 2720 (H–CO).

PMR spectrum (δ, ppm): 0.84 (m, 3H, CH_3-4), 1.27 (m, 6H, CH_2), 1.5-1.7 (m, 6H, $CH_3-C=C$), 1.7 (m, 1H, H-4), 2.0 (m, 2H, H-7), 2.3 (m, 2H, H-2), 5.2 (m, 1H, H-9), 9.5 (br.s, 1H, H-1).

1-Tosyloxy-4,8-dimethyldec-8Z/E-ene (7). At 20°C, with stirring, 0.65 g (0.017 mole) of $NaBH_4$ was added to a solution of 1.8 g (0.01 mole) of the aldehyde (6) in 20 ml of absolute methanol and then the reaction mixture was stirred for 2 h and was left for 12 h, after which 15 ml of 5% AcOH was added, the methanol was distilled off, the residue was extracted with diethyl ether, and the extract was washed successively with water and saturated solutions of Na_2CO_3 and NaCl, and was dried with $MgSO_4$. After evaporation, 1.7 g of a product (ν_{OH} 3300-3450 br.s) was obtained, and a solution of this in 2.8 ml of pyridine was treated at 0-5°C with 2.1 g (0.013 mole) of tosyl chloride. The reaction mixture was stirred for 5.5 h and was left at 8°C for 12 h. Then 40 ml of Et_2O was added to it and it was washed successively with 10% HCl and saturated solutions of Na_2CO_3 and NaCl, and dried with $MgSO_4$. After evaporation in vacuum, 2.8 g (83%) of the tosylate (7) was obtained.

IR spectrum (ν, cm^{-1}): 1600 ($C{=}C_{Ar}$).

PMR spectrum (δ, ppm): 0.8 (m, 3H, CH_3-4), 1.2 (m, 8H, CH_2), 1.5-1.7 (m, 6H, $CH_3-C=C$), 1.7 (m, 1H, H-4), 2.0 (m, 2H, H-7), 2.4 (s, 3H, CH_3-Ar), 3.96 (t, 2H, J = 6 Hz, H-1), 5.15 (m, 1H, H-9), 7.3 d and 7.75 d (4H, J = 8 Hz, CH_{Ar}).

3,7-Dimethylpentadec-2Z/E-ene (8). At −78°C with stirring under Ar, 2.5 ml of a 0.1 M solution of Li_2CuCl_4 in THF was added to a solution of 3.38 g (0.01 mole) of the tosylate (7) in 40 ml of absolute Et_2O, and then a solution of amylmagnesium bromide generated from 0.6 g (0.025 g-atom) of Mg and 2.8 g (0.018 mole) of $nC_5H_{11}Br$ (with CH_3I as initiator) was added dropwise, and the resulting reaction mixture was stirred at −70°C for 2 h and was left at room temperature for 12 h, after which 20 ml of Et_2O was added and the mixture was stirred for 0.5 h and poured into a cold saturated solution of NH_4Cl. The mixture was shaken vigorously, and then the organic layer was separated off and was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, and evaporated. The residue was chromatographed on 45 g of neutral Al_2O_3 (hexane–ether (9:1)). This gave 0.25 g of *n*-decane and 1.95 g (82%) of the alkene (8), n_D^{20} 1.4560. Its IR and PMR spectra were identical with those obtained in [10].

3,7-Dimethylpentadec-2-yl acetate (1), obtained with a yield of 76% from the alkene (**8**) as described in [10], had IR and PMR spectra identical with those of the authentic compound.

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