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SYNTHESIS OF DODECA-8E,10E-DIEN-1-OL — THE SEX PHEROMONE OF *Laspeyresia pomonella* VIA THE ACETOLYSIS OF 4-PROPENYL-1,3-DIOXANE

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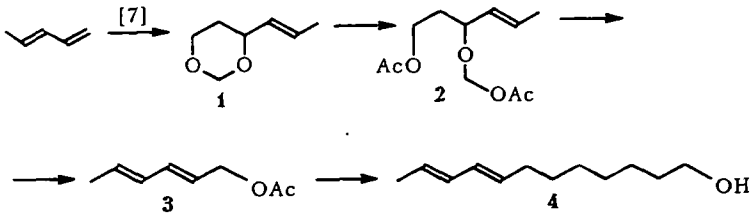
A new scheme has been developed for the synthesis of dodeca-8E,10E-dien-1-ol (the sex pheromone of the codling moth) from sorbyl acetate, available from 4-propenyl-1,3-dioxane through the intermediate diacetate of 3-propenyl-2-oxapentane-1,5-diol.

Dodeca-8E,10E-dien-1-ol (codlemone) (**4**) — the sex pheromone of the codling moth *Laspeyresia pomonella* L. — is one of the most studied of such compounds. Review papers [1-5] give a whole series of syntheses of this industrially important compound. The majority of the known preparative schemes for obtaining codlemone are based on the use as key synthons of derivatives of sorbic acid containing a ready-made conjugated (E,E)-dienic system [5, 6].

We have developed a new approach to the synthesis of the pheromone (**4**) from sorbyl acetate (**3**), which is available through selective transformations of 4-propenyl-1,3-dioxane (**1**) — a product of the utilization of piperylene, a waste from the manufacture of isoprene [7].

The acetolysis of the latter [8] to the diacetate of 3-propenyl-2-oxapentane-1,5-diol (**2**) and the subsequent elimination under acid conditions of the acetoxymethyl group in the form of paraformaldehyde and acetic acid, accompanied by the formation of a conjugated system of double bonds, led to the dienic acetate (**3**) [the chemical shift (q 18.11) of the C^6 atom in the ^{13}C NMR spectrum and also the magnitude (14.8 Hz) of the vicinal SSCC of the H-4 and H-5 protons showed the *trans*-configuration of the $C^4{=}C^5$ double bond, while the vicinal SSCC (15.1 Hz) of the H-2 and H-3 protons likewise showed the transoid nature of the $C^2{=}C^3$ bond], and this was converted into the desired codlemone by a Li_2CuCl_4-catalyzed cross-coupling reaction with the magnesium derivative of the tetrahydropyranyl (THP) ether of 6-chlorohexan-1-ol, according to [9], with an overall yield of 15%, calculated on the initial (**1**).



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in a film). PMR spectra (300 MHz) and ^{13}C NMR spectra (75.47 MHz) were recorded on a Bruker AM-300 instrument in $CDCl_3$ solution. Chromatographic analysis was conducted on a Chrom-5 chromatograph (stationary phase SE-30 silicone liquid, column length 1.2 m, working temperature 50-300°C) and

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also on a Shimadzu GC-9A instrument (stationary phase PEG-20M, quartz capillary column 0.2 × 25 m, carrier gas helium). TLC was conducted on Silufol plates with a fixed layer of SiO_2. The elementary analyses of the compounds synthesized agreed with the calculated figures.

Diacetate of 3-Propenyl-2-oxapentane-1,5-diol (2). In drops, a mixture of 25.5 g (0.25 mole) of Ac_2O and 0.13 ml of concentrated H_2SO_4 was added to 32.0 g (0.25 mole) of 4-propenyl-1,3-dioxane (**1**), obtained according to [7], whereupon the temperature of the mixture rose spontaneously to 60°C. After cooling to room temperature it was left to stand for 15 h. Then it was neutralized with crystalline AcONa, and the organic layer was separated off and was fractionally distilled to give 44.0 g (76%) of the diacetate (**2**), bp 123°C (4 mm), n_D^{20}, 1.4410 [8]. ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$): 17.10 (q, $CH_3C{=}C$), 20.19 and 20.30 (q, $\underline{C}H_3C$), 34.07 (t, C-4), 60.28 (t, C-5), 76.09 (d, C-3), 85.61 (t, C-1), 129.37 and 129.83 (d, C=C), 169.88 and 170.01 (s, MeCO).

Hexa-2E,4E-dien-1-yl Acetate (3). The reaction mixture was prepared by the addition of 3 ml of H_2SO_4 to 70.0 g (0.3 mole) of the diacetate (**2**). It was heated to 160°C and was distilled under reduced pressure (40 mm), a 55-125°C fraction being collected which was filtered from the precipitate of paraformaldehyde, diluted with Et_2O (200 ml), washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was distilled through an efficient laboratory fractionating column. This gave 14.4 g (33%) of sorbyl acetate (**3**), bp 36-37°C (4 mm), n_D^{20} 1.4740 [10] containing, according to capillary GLC, not less than 98% of the main (E,E)- isomer. PMR spectrum (300 MHz, $CDCl_3$): 1.77 (d, 3H, J = 6.7 Hz, H-6), 2.08 (s, 3H, CH_3CO), 4.57 (d, 2H, J = 6.7 Hz, H-1), 5.63 (dt, 1H, J = 15.1 and 6.7 Hz, H-2), 5.76 (dq, 1H, J = 14.8 and 7.6 Hz, H-5), 6.05 (dd, 1H, J = 14.8 and 10.6 Hz, H-4), 6.25 (dd, 1H, J = 15.1 and 10.6 Hz, H-3). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$): 18.11 (q, C-6), 20.91 (q, CH_3CO), 64.93 (t, C-1), 123.85 (d, C-3), 130.59 (d, C-4), 131.11 (d, C-2), 134.89 (d, C-5), 170.68 (s, $Me\underline{C}O$).

Dodeca-8E,10E-dien-1-ol (4). A solution of 1.02 g ($7.29 \cdot 10^{-3}$ mole) of the dienic acetate (**3**) in 10 ml of abs. THF (−10°C, argon) was treated with 1.5 ml of a 0.2 M solution of Li_2CuCl_4 in THF and then with a solution of a Grignard reagent prepared from 2.42 g ($11.0 \cdot 10^{-3}$ mole) of the THP ether of 6-chlorohexan-1-ol and 0.31 g ($12.8 \cdot 10^{-3}$ g-atom) of magnesium in 12 ml of THF. The mixture was kept at −10°C for 3 h, treated at 0°C with 10 ml of saturated NH_4Cl solution, and extracted with Et_2O (3 × 50 ml), and the extract was evaporated. The residue was dissolved in 22 ml of MeOH and, after the addition of 2.2 ml of water and 0.22 g of MeOH [sic], the mixture was heated at 60°C for 3 h and was then evaporated. The residue was diluted with Et_2O (30 ml), washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4, and evaporated. After column chromatography (SiO_2, pentane−Et_2O (4:1)) 0.74 g (60%) of the alcohol (**4**) was obtained (content of the E,E-isomer not less than 96% according to capillary GLC and ^{13}C NMR), mp 27.0-28.5°C, IR, PMR, and ^{13}C NMR spectra identical with those described in [11].

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