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New Synthesis of 3,7-Dimethylpentadec-2-yl Acetate Sex Pheromone of the Pine Sawfly *Neodiprion lecontei*

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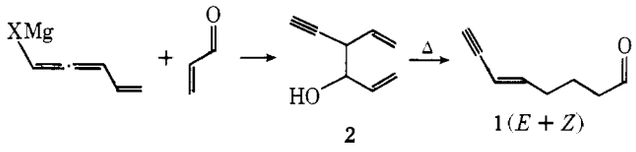
Recently,[1] we published a two-step synthetic sequence for aldehydes **1** by (i) the reaction of vinylallenic Grignard reagents with $\alpha\beta$-ethylenic ketones and (ii) the oxy-Cope transposition in refluxing diglyme of the resulting 4-ethynyl hexa-1,5-dien-3-ols **2** (Scheme I).

We report here an application of this sequence in the synthesis of the title pheromone **3** (*dl*), the structure of which was demonstrated by Coppel and co-workers in 1976.[2] A seven-step synthesis of **3** from 2,6-dimethylcyclohexanone was proposed very recently.[3]

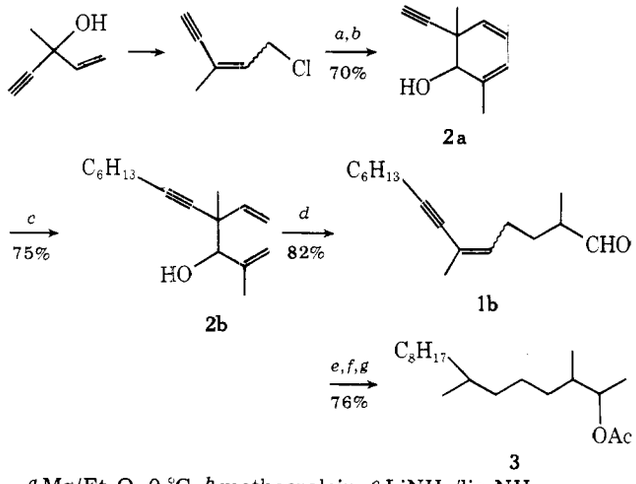
5-Chloro-3-methylpent-3-en-1-yne is readily prepared from 3-methylpent-4-en-1-yn-3-ol.[4] Its vinylallenic Grignard reagent reacts with methacrolein leading to alcohol **2a** which is easily alkylated by *n*-hexyl bromide using lithium amide in liquid ammonia. Heating of **2b** for 2 h in refluxing diglyme gives the fairly unstable aldehyde **1b**. After hydrogenation of **1b** the synthesis of **3** is terminated as outlined in Scheme II by reaction of methylmagnesium iodide with the corresponding saturated aldehyde. The overall yield from alcohol **2a** to the pheromone (identified by comparison of its spectra with those previously described) is 47%.

Scheme I



2 $1(E + Z)$

Scheme II



3

[a] Mg/Et_2O, 0 °C. [b] methacrolein. [c] $LiNH_2$/liq NH_3, $C_6H_{13}Br$. [d] diglyme reflux. [e] H_2, Pd/C 5%/AcOEt. [f] CH_3MgI/Et_2O. [g] Ac_2O.

Experimental Section[5]

The starting 3-methylpent-4-en-1-yn-3-ol was kindly provided by Dr. Pesnelle from Sté Roure-Bertrand.

2,4-Dimethyl-4-ethynylhexa-1,5-dien-3-ol (2a). The Grignard reagent of 11.5 g (0.1 mol) of 5-chloropent-3-en-1-yne is prepared and condensed with 7 g (0.1 mol) of methacrolein following published procedure;[1] 10.5 g (70%) of **2a** ($E_{0.2}$ = 47–48°) are obtained: IR (neat liq) 3550, 3450, 3300, 3080, 3060, 3010, 2100, and 1640 cm^{-1}; NMR (CCl_4) δ 1.20 and 1.28 (3 H, 2 s corresponding to threo and erythro isomers 1/1), 1.74 and 1.77 (3 H, 2t, J = 1.5 Hz), 2.30 (1 H, s), 2.52 (1 H, s, exchange with D_2O), 3.81 (1 H, s), 4.7–6.1 (5 H, M); mass spectrum 150 $M^{+\cdot}$ (1), 79 (100). Anal. Calcd: C, 79.95; H, 9.39. Found: C, 79.75; H, 9.71.

2,4-Dimethyl-4-vinyldodec-1-en-5-yn-3-ol (2b). Alcohol **2a** (10.5 g, 0.07 mol) is added after 5 min to a solution cooled to −45 °C of 0.15 mol of lithiumamide in 150 mL of liquid ammonia (freshly prepared from 1.0 g of lithium). *n*-Hexyl bromide (12.5 g, 0.075 mol) is then added after 10 min and the reaction mixture is stirred for 5 h at −45 °C. After addition of 200 mL of ether, ammonia is slowly evaporated. The residue is hydrolyzed by 200 mL of crushed ice and the solution was extracted with ether. The organic layer is washed until neutral and dried over $MgSO_4$. Evaporation of solvent leaves 15 g of crude material which by chromatography over silica gel (eluant petroleum ether–ether 4:1) gives 11.5 g (75%) of **2b** contaminated with about 10% aldehyde **1b**. This aldehyde seems to be formed during purification and complicates isolation of pure **2b** on a large scale: IR (neat liq) 3550, 3450, 3080, 3010, and 1640 cm^{-1}; NMR (CCl_4) δ 0.87 (3 H, t), 1.0–1.6 (11 H, M), 1.75 (3 H, M), 2.0 (1 H, M exchange with D_2O), 2.20 (2 H, M), 3.8 (1 H, broad s), 4.7–6.1 (5 H, M).

2,6-Dimethyltetradec-5-en-7-ynal (1b). A solution of 4.4 g (0.019 mol) of alcohol **2b** (contamined with ~10% of **1b**) in 100 mL of diglyme is refluxed for 2.25 h. After cooling, 400 mL of ether is added; the resulting solution is washed 15 times with 30 mL of water in order to eliminate diglyme and dried over $CaCl_2$. The unstable aldehyde (3.6 g 82%) is purified by chromatography over silica gel (eluent petroleum ether–ether 9:1) after removal of the solvent: IR (neat liq) 3010, 2700, 2220, 1730, 1670, and 1630 cm^{-1}; NMR (CCl_4) δ 0.89 (3 H, t), 1.05 (3 H, d, J = 7 Hz), 1.15–1.70 (13 H, M), 1.80–2.40 (5 H, M), 5.5 (1 H, M), 9.70 (1 H, d, J = 1 Hz); mass spectrum m/e 234 $M^{+\cdot}$ (20), 164 (99), 93 (100).

2,6-Dimethyltetradecanal. Aldehyde **1b** (2 g, 0.085 mol) in 30 mL of ethyl acetate is hydrogenated at ordinary pressure using 5% Pd/C as catalyst. After filtration and evaporation of solvent, 1.88 g (94%) of saturated aldehyde are obtained, pure enough (TLC) to be used without further purification: IR (neat liq) 2700, 1725 cm^{-1}; NMR (CCl_4) δ 0.9 (6 H, M), 1.05 (3 H, D, J = 7 Hz), 1.1–2.4 (20 H, M), 9.62 (1 H, d, J = 1 Hz); mass spectrum m/e 240 $M^{+\cdot}$ (0.5), 57 (100).

3,7-Dimethylpentadec-2-yl acetate (3). The Grignard reagent is prepared from 1.42 g (0.01 mol) of methyl iodide, 0.36 g (0.015 g-atom) of magnesium, and 10 mL of anhydrous ether. To the magnetically stirred solution is added at 0 °C 1.34 g (0.006 mol) of the saturated aldehyde dissolved in 5 mL of ether. After 20 min of stirring at 0 °C, 2 g (0.02 mol) of acetic anhydride in 2 mL of ether is dropped into the mixture which is hydrolyzed by 20 mL of a saturated solution of NH_4Cl 20 min after the end of the addition. The organic layer is separated, washed with 3 × 20 mL of H_2O, and dried over $CaCl_2$. The pheromone is, after removal of the solvent, purified by chromatography over silica gel (eluent: petroleum ether–ether 9:1) and 1.35 g (81%) of **3** is obtained: IR (neat liq) 1735, 1240 (identical to one described (**3**)) cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (9 H, M), 1.0–1.7 (25 H, M), 1.97 (3 H, s), 4.80 (1 H, M); ^{13}C NMR ($CDCl_3$) δ 170.5)s), 74.24 (d), 74.03 (d), 73.95 (d), 24 peaks between 37.6 and 14.1; mass spectrum m/e 298 $M^{+\cdot}$ (0), 255 (5), 254 (11), 238 (33), 116 (14), 87 (45), 44 (55), 43 (100). Anal. Calcd: C, 76.45; H, 12.83. Found: C, 76.03; H, 12.66. All the prominent peaks were also described by Coppel et al.[2]

Registry No.—**1b**, 64682-96-8; *erythro*-**2a**, 64682-97-9; *threo*-**2a**, 64682-98-0; **2b**, 64728-32-1; **3**, 59056-74-5; hexyl bromide, 111-25-1; 2,6-dimethyltetradecanal, 64682-99-1.

References and Notes

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(5) Infrared spectra were determined using a Perkin-Elmer Model 257; NMR spectra were measured in a Varian Associates Model A-60 or XL-100 spectrometer with solvent as specified. Mass spectra were observed using Varian Associates Model CH-5 spectrometer at 70 eV by direct inlet.

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