

## New synthesis of (*E*)-3,7-dimethyl-2,7-octadienylpropionate and (*E*)-3,7-dimethyl-2-octen-1,8-diol, pheromone components of San Jose scale-insect *Quadraspidiotus perniciosus* and african monarch butterfly *Danaus chrysippus*

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**Abstract.** 6-Methyl-6-hepten-2-one (**3**) on reaction with ethyl  $\alpha$ -dimethylphosphonate/NaH gives a mixture of (*E*)- and (*Z*)-conjugated esters. The major (*E*)-isomer, (*E*)-ethyl-3,7-dimethyl-2,7-octadienoate (**4**), on reduction with  $\text{LiAlH}_4$  at room temperature furnishes (*E*)-3,7-dimethyl-2,7-octadien-1-ol (**5**) which on propionylation affords (*E*)-3,7-dimethyl-2,7-octadienyl propionate (**1**). Carbinol (**5**) is converted into its silyl ether (*E*)-2,6-dimethyl-8-*t*-butyldimethylsilyloxy-1,6-octadiene (**6**) with *t*-Bu(Me) $_2$ SiCl in  $\text{CH}_2\text{Cl}_2$ , which on hydroboronation-oxidation with 9-BBN/NaOH– $\text{H}_2\text{O}_2$  followed by disilylation with  $(n\text{-Bu})_4\text{N}^+\text{F}^-$  at room temperature, gives (*E*)-3,7-dimethyl-2-octen-1,8-diol (**2**).

**Keywords.** Pheromones; hydroboration-oxidation; 9-BBN/ $\text{H}_2\text{O}_2$ –NaOH.

### 1. Introduction

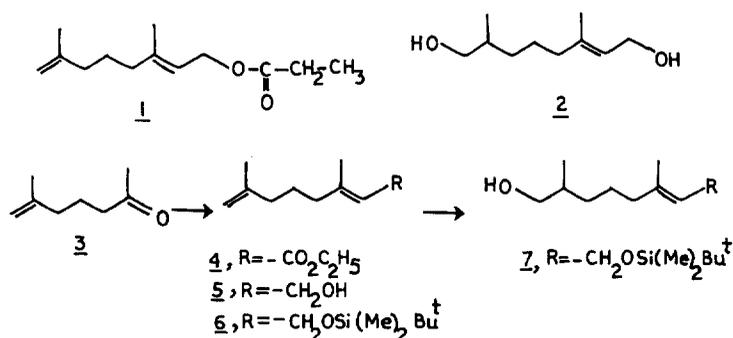
Anderson *et al* (1981) isolated an active component from San Jose scale-insect *Quadraspidiotus perniciosus* and assigned structure (**1**) to it on the basis of spectral evidence. (*E*)-3,7-dimethyl-2-octen-1,8-diol (**2**), an active component of *Danaus chrysippus* (african monarch butterfly) was isolated by Meinwald *et al* (1971) and identified as **2** on the basis of spectral studies. Alderdice *et al* (1984) and Novak *et al* (1985) have reported the synthesis of **1** whereas Bidan *et al* (1977), Fuijisawa *et al* (1982) and Julia and Verpeaux (1983) have reported the synthesis of **2**. Recently, Ferroud *et al* (1986) have synthesised both these pheromones. But most of these syntheses of **1** and **2** involve multistep sequences leading to low yields. We report herein a simple synthesis of **1** and **2** using the intermediate (**3**) reported earlier by us (Trehan *et al* 1986).

### 2. Results and discussion

The reaction strategy utilised in the synthesis of **1** and **2** is discussed in scheme 1.

Base-catalysed condensation of **3** with ethyl  $\alpha$ -dimethylphosphonate in the presence of NaH/THF resulted in a mixture of (*E*)- and (*Z*)-isomers of the conjugated ester from which the pure (*E*)-isomer (**4**) was separated and reduced with  $\text{LiAlH}_4$  in anhydrous ether at room temperature to furnish the carbinol (**5**). Reaction of **5** with

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Scheme 1.

propionyl chloride in the presence of triethylamine in CH<sub>2</sub>Cl<sub>2</sub> led to **1** in 83.33% yield. For the synthesis of **2**, carbinol (**5**) was treated with Bu<sup>t</sup>(Me)<sub>2</sub>SiCl in anhydrous CH<sub>2</sub>Cl<sub>2</sub> containing Et<sub>3</sub>N to get *t*-butyldimethylsilyl ether (**6**) which on hydroboration with 9-9-borabicyclo [3.3.1] nonane (9-BBN) in THF at room temperature followed by oxidation with alkaline hydrogen peroxide (Ferroud *et al* 1986) furnished the alcohol (**7**) as light yellow oil. Desilylation of **7** with tetra-*n*-butylammonium fluoride in THF afforded the diol (**2**) in 86.8% yield. The IR and the PMR spectral data of pheromones **1** and **2** are consistent with those reported for them in literature.

### 3. Experimental

The boiling points are uncorrected. Progress of all the reactions was monitored by TLC using silica gel impregnated with 13% calcium sulphate. Silica gel (Achme' 60-80 mesh) was used for column chromatography. The IR spectra ( $\nu_{\max}$  in cm<sup>-1</sup>) were run on a Perkin-Elmer 337 spectrophotometer and 90 MHz PMR spectra on an EM-390 instrument using TMS as the internal standard. Unless otherwise stated, all organic extracts were dried over anhydrous sodium sulphate.

#### 3.1 (*E*)-ethyl-3,7-dimethyl-2,7-octadienoate (**4**)

To a well-stirred suspension of sodium hydride (1.66 g, 69.17 mmol) in anhydrous THF (25 ml), ethyl  $\alpha$ -dimethylphosphonate (6.52 g, 33.33 mmol) in THF (25 ml) was added dropwise at a temperature below 20°. Stirring was continued till the evolution of gas ceased. The reaction mixture was chilled in ice and a solution of 6-methyl-6-hepten-2-one (**3**) (3.5 g, 27.77 mmol) (Trehan *et al* 1986) in anhydrous THF (15 ml) was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred for another 2 h and left overnight. It was then stirred for 4 h at 70°, cooled to room temperature, decomposed with water (40 ml), extracted with ether (4 × 50 ml) and dried. Solvent evaporation followed by column chromatography (Silica gel, petroleum ether-ether 9:1) afforded **4** (2.69 g, 49.5% yield); IR: 1715, 1650 and 840 cm<sup>-1</sup>; PMR (CCl<sub>4</sub>):  $\delta$  5.53 (1H, s, olefinic proton), 4.60 (2H, s, H<sub>2</sub>C=C-), 4.0 (2H, q, -OCH<sub>2</sub>-), 2.2-1.86 (7H, m + s, allylic 2x-CH<sub>2</sub>-, C<sub>3</sub>-CH<sub>3</sub>), 1.7-1.46 (5H, bs, C<sub>7</sub>-CH<sub>3</sub>, saturated -CH<sub>2</sub>) and 1.23 (3H, t, -CH<sub>2</sub>-CH<sub>3</sub>). (Found: C, 73.25; H, 10.0. C<sub>12</sub>H<sub>20</sub>O<sub>2</sub> requires C, 73.47; H, 10.20%).

3.2 (*E*)-ethyl-3,7-dimethyl-2,7-octadien-1-ol (5)

A solution of 4 (2.5 g, 12.75 mmol) in anhydrous ether (20 ml) was added dropwise to a suspension of lithium aluminium hydride (0.625 g, 16.44 mmol) in ether (25 ml) at 0°. After the addition was complete, the resulting mixture was stirred overnight at ambient temperature, decomposed with a saturated solution of sodium potassium tartrate, extracted with ether (3 × 50 ml) and dried. Solvent removal followed by distillation under reduced pressure furnished 5 (1.2 g, 61.22% yield); b.p. 96–98°/15–16 mm; IR: 3300, 1050 and 840 cm<sup>-1</sup>; PMR(CCl<sub>4</sub>): δ 5.44 (1H, *t*, olefinic proton), 4.74 (2H, *s*, H<sub>2</sub>C=C-), 4.09 (2H, *d*, -H<sub>2</sub>COH), 2.93 (1H, *s*, -OH exchangeable with D<sub>2</sub>O), 2.07 (4H, *t*, allylic 2 × -CH<sub>2</sub>-) and 1.8–1.4 (8H, *bs*, C<sub>3</sub> & C<sub>7</sub>-CH<sub>3</sub>, saturated -CH<sub>2</sub>-). (Found: C, 77.71; H, 11.45. C<sub>10</sub>H<sub>18</sub>O requires C, 77.92; H, 11.69%).

3.3 (*E*)-3,7-dimethyl-2,7-octadienyl propionate (1)

To a well-stirred and cooled solution of 5 (1.1 g, 7.14 mmol) and triethylamine (1.44 g, 14.26 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 ml) was added dropwise a solution of propionyl chloride (0.726 g, 7.85 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The resulting solution was stirred for 1 h at 0°C and left overnight. Water (10 ml) was added to the reaction mixture which was then extracted with ether (4 × 50 ml). Removal of the solvent followed by column chromatography on silica gel using petroleum ether–ether (9:1) furnished 1 (1.25 g, 83.33% yield); IR: 3010, 2920, 1730, 1670, 1640, 1450, 1220, 1170, 1010, 880, 840 and 805 cm<sup>-1</sup>; PMR(CCl<sub>4</sub>): δ 5.36 (1H, *t*, olefinic proton), 4.70 (2H, *bs*, H<sub>2</sub>C=C-), 4.53 (2H, *d*, -CH<sub>2</sub>-O-), 2.36–1.8 (6H, *m*, allylic 2 × -CH<sub>2</sub>-, -CO-CH<sub>2</sub>-), 1.7–1.5 (8H, *s* + *m*, allylic 2 × -CH<sub>3</sub>, saturated -CH<sub>2</sub>-) and 1.10 (3H, *t*, -CH<sub>2</sub>-CH<sub>3</sub>). (Found: C, 73.99; H, 10.21. C<sub>13</sub>H<sub>22</sub>O<sub>2</sub> requires C, 74.28; H, 10.47%).

3.4 (*E*)-2,6-dimethyl-8-*t*-butyldimethylsilyloxy-1,6-octadiene (6)

To a well-cooled solution of 5 (1.0 g, 6.48 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) containing Et<sub>3</sub>N (1.31 g, 12.99 mmol) a solution of *t*-Bu (Me)<sub>2</sub>Cl (1.17 g, 7.79 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at 0°C was added dropwise with stirring and the resulting mixture stirred for another 1 h at 0°C and left overnight. The reaction mixture was poured into water, extracted with ether (4 × 50 ml), washed with brine (2 × 25 ml), dried and concentrated *in vacuo*. The residue was chromatographed on a silica gel column using petroleum ether–ether (24:1) to afford 6 (1.18 g, 67.10% yield); IR: 3010, 2920, 1670, 1645, 1468, 1360, 1250, 1080, 880 and 840 cm<sup>-1</sup>; PMR(CCl<sub>4</sub>): δ 5.30 (1H, *t*, olefinic proton), 4.73 (2H, *bs*, H<sub>2</sub>C=C-), 4.16 (2H, *d*, -H<sub>2</sub>C-O-), 2.01–1.73 (4H, *m*, allylic 2 × -CH<sub>2</sub>-), 1.7–1.5 (8H, *2s*, allylic 2 × -CH<sub>3</sub>, saturated -CH<sub>2</sub>-), 0.90 (9H, *s*, -Si(CH<sub>3</sub>)<sub>3</sub>) and 0.01 (6H, *s*, Si(CH<sub>3</sub>)<sub>2</sub>). (Found: C, 71.50; H, 11.78. C<sub>16</sub>H<sub>32</sub>O requires C, 71.64; H, 11.94%).

3.5 (*E*)-2,6-dimethyl-8-*t*-butyldimethylsilyloxy-6-octen-1-ol (7)

To a solution of 9-borabicyclo[3.3.1]nonane (0.451 g, 3.73 mmol) in THF (5 ml) was added a solution of 6 (0.50 g, 1.86 mmol) in THF (10 ml) at 25° with stirring. After the completion of hydroboration (TLC monitoring), 6 M NaOH (1.85 ml) followed by 30% H<sub>2</sub>O<sub>2</sub> (1.5 ml) was added slowly and the reaction mixture heated for 1 h at 60°. This was cooled to 25°, extracted with ether (4 × 25 ml) after saturating the aqueous

layer with  $K_2CO_3$  and dried. Removal of the solvent, followed by chromatography over silica gel using petroleum ether–ether (7:3) afforded **7** (0.264 g, 49.5% yield) as yellow oil; IR: 3400–3300, 1050 and  $840\text{ cm}^{-1}$ ; PMR( $CCl_4$ ):  $\delta$  5.30 (1H, *t*, olefinic proton), 4.16 (2H, *d*,  $-\underline{CH}_2-\underline{O}-$ ), 3.50 (2H, *d*,  $-\underline{H}_2C-\underline{OH}$ ), 2.60 (1H, *s*,  $-\underline{OH}$  exchangeable with  $D_2O$ ), 2.06–1.90 (2H, *m*, allylic  $-\underline{CH}_2-$ ), 1.63 (3H, *s*, allylic  $-\underline{CH}_3$ ), 1.55–1.46 (5H, *bs*, saturated  $2 \times -\underline{CH}_2-$ ,  $\underline{HO}-\underline{CH}_2-\underline{CH}-$ ), 1.1 (3H, *d*,  $-\underline{CH}_3$ ), 0.89 (9H, *s*,  $-\underline{Si}(\underline{CH}_3)_3$ ) and 0.01 (6H, *s*,  $-\underline{Si}(\underline{CH}_3)_2$ ). (Found: C, 66.82; H, 11.54.  $C_{16}H_{34}O_2Si$  requires C, 67.13; H, 11.89%).

### 3.6 (*E*)-3,7-dimethyl-2-octen-1,8-diol (**2**)

To a stirred solution of **7** (0.260 g, 0.91 mmol) in THF (10 ml) was added tetra *n*-butylammonium fluoride (0.251 g, 1.0 mmol) in THF (5 ml) at ambient temperature and the reaction mixture was left overnight with stirring. Water (10 ml) was added, the solution extracted with ether ( $4 \times 25\text{ ml}$ ), and the organic extract washed with water ( $2 \times 20\text{ ml}$ ) and dried. Evaporation of the solvent followed by chromatography over silica gel gave pure **2** (0.135 g, 86.8% yield) after elution with petroleum ether–ether (3:2); IR: 3400–3300, 3010, 2920, 1670, 1360, 1265, 1050 and  $840\text{ cm}^{-1}$ ; PMR ( $CCl_4$ ):  $\delta$  5.3 (1H, *t*, olefinic proton), 4.10 (2H, *d*,  $=\underline{CH}-\underline{CH}_2-\underline{OH}$ ), 3.5 (2H, *d*,  $-\underline{CH}_2\text{OH}$ ), 2.6 (2H, *bs*,  $2 \times -\underline{OH}$  exchangeable with  $D_2O$ ), 2.1 (2H, *t*, allylic  $-\underline{CH}_2-$ ), 1.70 (3H, *s*, allylic  $-\underline{CH}_3$ ), 1.5–1.43 (5H, *bs*, saturated  $2 \times -\underline{CH}_2-$ ,  $\underline{HO}-\underline{CH}_2-\underline{CH}-$ ) and 1.03 (3H, *d*,  $-\underline{CH}_3$ ). (Found: C, 69.54; H, 11.39.  $C_{10}H_{20}O_2$  requires C, 69.77; H, 11.63%).

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