

## Supporting information

### A Novel Approach to Timberwood Fragrances

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#### Chemicals

All solvents, catalyst and other chemicals were used without further purification. Supported palladium and platinum catalysts and Ca/Na on silica were purchased from Evonik.

All reactions were carried out under argon. The crude products were analyzed by GC with internal standard and quantitative NMR.

#### Analytatics:

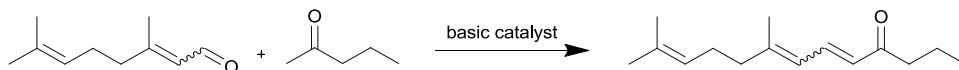
##### GC

The reactions were monitored by GC on a HP ChemServer4930 using an OPTIMA δ3, methyl-phenyl-polysiloxane block polymers column (30 m x 0.32 mm, film thickness: 0.25 μm), and a FID detector using helium as a carrier gas. Injector (split) temperature: 250 °C; detector temperature: 300 °C; split proportion: 1:50; column pressure: 1.5 ml constant flow at 7.68 psi; injection volume: 1.0 μl; column temperature (aldol condensation): 60 °C to 250 °C at 8 °C/min, stay at 250 °C for 8 min, 250 °C to 300 °C at 6 °C/min, stay at 300 °C for 1.67 min. Column temperature (cyclization and hydrogenation): 60 °C to 250 °C at 8 °C/min, stay at 250 °C for 8 min, 250 °C to 300 °C at 8 °C/min and stay at 300 °C for 2 min.

##### NMR:

NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. <sup>1</sup>H-NMR spectra were recorded at 300 MHz, <sup>13</sup>C spectra were recorded at 75 MHz, respectively. The quantitative spectra were recorded in CDCl<sub>3</sub> using 1,4 dimethoxybenzene as internal standard. The delay d1 between two pulses was set to 30 s. 12 – 25 mg samples were used.

#### Aldol condensation



Citral (2.0 g, purity: 95.0%, 12.5 mmol) and 2-pentanone (20 g, purity: 99.0%, 229.9 mmol) were stirred under argon in a 2-neck-flask at 80 °C. Afterwards, Ca/Na on silica

(360 mg, 18 wt% on citral) was added. The mixture was stirred for 4 h at 80 °C. After cooling to room temperature the mixture was filtered, the heterogeneous catalyst washed with 2-pentanone and all volatiles of the liquid phase were removed in vacuo (20 mbar, 40 °C). Yield: 87.5% (2.90 g, purity: 83.1%, determined by GC, *E/Z*-mixture).

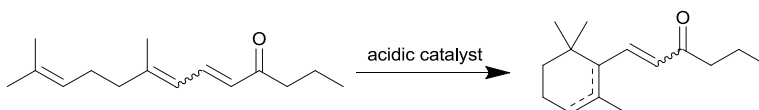
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.47 (dd, *J* = 11.5 Hz, 14.2 Hz, HC(6)); 7.44 (dd, *J* = 11.5 Hz, 15.2 Hz, HC(6)); 6.11 (d, *J* = 15.3 Hz, HC(5) or HC(7)); 6.07 (d, *J* = 15.2 Hz, HC(5) or HC(7)); 5.99 (d, *J* = 11.4 Hz, HC(5) or HC(7)); 5.12 (m, HC(11)); 2.53 (t, *J* = 7.3 Hz, H<sub>2</sub>C(3) or H<sub>2</sub>C(9)); 2.52 (t, *J* = 7.2 Hz, H<sub>2</sub>C(3) or H<sub>2</sub>C(9)); 2.32 (t, *J* = 7.9 Hz, H<sub>2</sub>C(3) or H<sub>2</sub>C(9)); 2.16 (s, CH<sub>3</sub>), 1.90 (s, CH<sub>3</sub>), 1.68 (m, CH<sub>2</sub>, H<sub>2</sub>C(2) and H<sub>2</sub>C(10)); 1.61 (s, CH<sub>3</sub>), 0.95 (t, *J* = 7.4 Hz, H<sub>3</sub>C(1));

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ = 201.0 (CO), 150.9 (C=C), 150.9 (C=C), 138.6 (C=C), 138.4 (C=C), 132.6 (C=C), 132.2 (C=C), 127.6 (C=C), 127.4 (C=C), 124.7 (C=C), 123.8 (C=C), 123.3 (C=C), 123.2 (C=C), 42.8, 42.7, 40.4, 33.0, 26.9, 26.3, 25.7, 24.6, 18.0, 17.9, 17.7, 17.5, 13.9.

The <sup>1</sup>H-NMR data is in accordance to literature data.<sup>1</sup> To the best to our knowledge no <sup>13</sup>C-NMR data on 8,12-dimethyl-5,7,11-tridecatrien-4-one was published before.

## Cyclization

### Example 1



8,12-Dimethyl-5,7,11-tridecatrien-4-one (10.0 g, purity: 86.7%, < 5% citral, the remaining < 8.3% are unidentified by-products with each < 2%, 39 mmol) was added dropwise to 50 ml H<sub>3</sub>PO<sub>4</sub> (aq., 85%) at room temperature. The temperature rose during the addition from 23-24°C to 32-33°C. After completion the mixture was stirred for additional 40 min at room temperature. The mixture was poured on 50 g ice and the organic phase was extracted with ethyl acetate (3 x 50 ml). The combined organic phases were washed with 70 ml water and 70 ml saturated aqueous NaHCO<sub>3</sub> solution, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated in vacuo. The raw product (9.9 g) was vacuum distilled (96-97 °C, 3.1 x 10<sup>-1</sup> mbar). Yield: 56.4% (6.9 g, purity: 70.4% α-product and 13.8% β-product, determined by GC, *E/Z*-mixture).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.63 (dd, *J* = 9.7 Hz, 15.8 Hz, HC(1)); 6.09 (d, *J* = 15.1 Hz, HC(2)); 5.49 (br, HC(3')); 2.53 (t, *J* = 7.5 Hz, H<sub>2</sub>C(4)); 2.27 (d, *J* = 9.7 Hz, HC(1')); 2.04 (m, CH<sub>2</sub>), 1.3-1.1 (m, 7 H); 0.95 (t, *J* = 7.2 Hz, H<sub>3</sub>C(6)); 0.93 (s, H<sub>3</sub>C(6)); 0.87 (s, H<sub>3</sub>C-C(6'));

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ = 200.6 (CO), 147.8 (C=C), 132.0 (C=C), 131.6 (C=C), 122.5 (C=C), 54.3, 41.9, 32.5, 31.2, 27.8, 26.8, 23.0, 22.8, 17.8, 13.8.

<sup>1</sup> E. Galera and A. Zabža, *Bull. De L'Acad. Pol. Des Sciences*, 1977, **25(8)**, 615.

### Example 2:

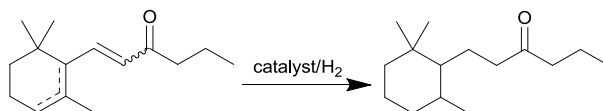
A solution of 8,12-dimethyl-5,7,11-tridecatrien-4-one (15.0 g, purity: 86.7%, < 5% citral, the remaining < 8.3% are unidentified by-products with each < 2%, 59 mmol) in 15 ml heptane was cooled to -6 °C and added dropwise to a mixture of 47 g H<sub>2</sub>SO<sub>4</sub> (96%) and 45 ml heptane at -10 – 20 °C. The reaction mixture was stirred mechanically with 600 r/min. After 20 min the addition was completed and the mixture stirred for additional 60 min. During this time the mixture was slowly warmed to 0 °C. The reaction mixture was poured on 80 g ice and the aqueous phase was separated and extracted with heptane (2 x 35 ml). The combined organic phases were washed with 40 ml saturated aqueous NaCl solution, 40 ml saturated aqueous NaHCO<sub>3</sub> solution, saturated aqueous NaCl solution (3 x 35 ml, until the aqueous phase became neutral), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated in vacuo. The raw product (14.6 g) was vacuum distilled (98-102 °C, 2.0 x 10<sup>-1</sup> mbar). Yield: 51.9% (8.1 g, purity: 83.4% β-product, determined by GC, *E/Z*-mixture).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.29 (dd, *J* = 16.4 Hz, HC(1)); 6.13 (d, *J* = 16.3 Hz, HC(2)); 2.55 (t, *J* = 7.3 Hz, H<sub>2</sub>C(4)); 2.17 (dd, *J* = 6.2 Hz, H<sub>2</sub>C(3')); 1.76 (s, H<sub>3</sub>C-C(2')), 1.69 (m, H<sub>2</sub>C(5)), 1.65 (m H<sub>2</sub>C(4') or H<sub>2</sub>C(5')); 1.18 (s, 6H, H<sub>3</sub>C-C(6')); 0.96 (t, *J* = 7.4 Hz, H<sub>3</sub>C(6));

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ = 200.9 (CO), 142.0 (C=C), 136.1 (C=C), 135.7 (C=C), 130.7 (C=C), 42.5, 39.7, 34.1, 33.5, 28.8, 22.7, 21.7, 18.9, 18.0, 13.9.

To the best to our knowledge no NMR data on both isomers was published before.

### Hydrogenation



A solution of 1-(2,2,6-trimethylcyclohex-2-en-1-yl)-1-hexen-3-one (3 g, purity: 87.5 %, < 4% 8,12-dimethyl-5,7,11-tridecatrien-4-one, the remaining < 8.5% are unidentified by-products with each < 1%, 12 mmol) and 35 ml cyclohexane was purged with hydrogen in a two-neck flask with 250 mg palladium on carbon (10% Pd on C). The mixture was stirred at room temperature under a hydrogen atmosphere (1 bar) for 16 h. Initially the temperature rose from 25 °C to 29 °C. After 60 min reaction time the temperature decreased to 25 °C. The mixture was filtered and the solvent removed in vacuo. Yield: 91.2 % (3.1 g, purity: 78.6% determined by GC, the product is a mixture of diastereomeres).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.37 (t, *J* = 7.5 Hz and 7.2 Hz, H<sub>2</sub>C(4) and H<sub>2</sub>C(2)); 2.0 – 0.8 (m, 26 H);

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ = 211.6 (CO), 49.2, 44.7, 34.3, 30.3, 19.4, 17.3, 13.8.

The <sup>1</sup>H-NMR data is in accordance to literature data.<sup>2</sup> To the best to our knowledge no <sup>13</sup>C-NMR data on 1-(2,2,6-trimethylcyclohex-1-yl)-hexan-3-one was published before.

<sup>2</sup> K.-H. Schulte-Elte, W. Giersch, B. Winter, H. Pamingle and G. Ohloff, *Helv. Chim. Acta*, 1985, **68**, 1961.

## NMR spectra

