

Supplementary Information

An Unusual Dimerization of Primary Unsaturated Alcohols Catalyzed by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$

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General Information: ^1H -NMR spectra were recorded with a JOEL JMN-500 (500 MHz) spectrometer in CDCl_3 and are referenced at 7.24 ppm for CDCl_3 . ^{13}C -NMR spectra were recorded with a JOEL JMN-500 (125 MHz) spectrometer in CDCl_3 and are referenced at 77 ppm for CDCl_3 . Chemical shifts are given in ppm. Conventional mass spectra were obtained on a Shimadzu GCMS-QP 5050A instrument and high resolution mass spectra were recorded with a JEOL JMS-700 spectrometer. Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. The products were purified by flash chromatography on silica gel (Nacalai Tesque Inc., Silica Gel 60, 230-400 mesh) and/or preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) equipped with GPC columns using CHCl_3 as an eluent. $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ was prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ according to the reported procedure.¹ Other reagents except triisopropylsiloxy-5-hexene (**1h**) were commercially available and used without further purification. 1-Hexanol, 3-hexanone (**5**) and 1-decanal (**7**) are commercially available and the ^1H - and ^{13}C -NMR spectra are consistent with those of the authentic sample.

1-Triisopropylsiloxy-5-hexene (1h). To a mixture of **1a** (1.52 g, 15.2 mmol), triethylamine (2.9 mL, 20.8 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in THF (30 mL) was added a solution of triisopropylsilyl chloride (3.50 g, 18.2 mmol) in THF (10 mL) over 3 min at 0 °C. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with hexane and the resulting ammonium salts were filtered with suction. The filtrate was concentrated and purification by flash chromatography on silica gel (hexane only) afforded **1h** (3.5 g,

90 %) as a colorless oil. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 1.01-1.09 (m, 21H), 1.40-1.48 (m, 2H), 1.50-1.57 (m, 2H), 2.01-2.09 (m, 2H), 3.66 (t, 2H, $J = 6.6$ Hz), 4.90-4.94 (m, 1H), 4.95-5.01 (m, 1H), 5.80 (ddt, 1H, $J = 17.0, 10.1, 6.8$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 12.0, 18.0, 25.2, 32.5, 33.6, 63.2, 114.3, 138.9.

General Procedure for Dimerization of Primary Unsaturated Alcohols.

5-Hydroxymethyl-6-undecanone (2a). Benzene (3.0 mL), 5-hexene-1-ol (**1a**) (103 mg, 1.03 mmol) and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (47.8 mg, 0.048 mmol) were placed in a 10 mL two-necked flask equipped with a reflux condenser and a magnetic stirring bar under N_2 atmosphere. The mixture was refluxed with stirring for 13 h. After the solvent was removed, the residue was purified by column chromatography on silica gel (2%, 3%, 4%, 5%, 6%, 7%, 8%, 10%, 15% AcOEt/hexane eluent). The 5% AcOEt/hexane eluent contained **2a**, which was purified further by preparative HPLC (58.9 mg, 59%): $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 0.87 (t, 6H, $J = 7.1$ Hz), 1.17-1.35 (m, 8H), 1.41-1.50 (m, 1H), 1.52-1.62 (m, 3H), 2.46 (dt, 2H, $J = 2.9, 7.3$ Hz), 2.66 (dq, 1H, $J = 3.9, 7.3$ Hz), 3.67 (dd, 1H, $J = 3.9, 11$ Hz), 3.75 (dd, 1H, $J = 7.3, 11$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 13.8, 13.8, 22.4, 22.7, 23.0, 27.9, 29.4, 31.3, 42.8, 53.6, 62.8, 215.3; IR (CDCl_3) 3438 cm^{-1} ($\nu_{\text{O-H}}$), 1705 cm^{-1} ($\nu_{\text{C=O}}$); EIMS (relative intensity) m/z 200 (M^+ , 10), 144 (39), 129 (17), 117 (100), 99 (39), 88 (51), 84 (48), 71 (35), 55 (65); HRMS (EI) (m/z) calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2$ (M^+) 200.1776, found: 200.1768.

Reaction of 1a Using a Shorter Reaction Time. Benzene (3.0 mL), **1a** (104 mg, 1.04 mmol) and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (45.8 mg, 0.0481 mmol) were placed in a 10 mL two-necked flask equipped with a reflux condenser and a magnetic stirring bar under N_2 atmosphere. The mixture was refluxed with stirring for 1 h. After the solvent was removed, the residue was purified by column chromatography on silica gel (2%, 3%, 4%, 5%, 6%, 7%, 8%, 10%, 15% AcOEt/hexane eluent). The 5% AcOEt/hexane eluent contained **2a**, **3a** and triphenyl phosphine derivatives (67.9 mg). Further purification by preparative HPLC gave **2a** and **3a** as an inseparable mixture (42.7 mg, 41%) in the ratio of 80 : 20 ($^1\text{H-NMR}$). The 15% AcOEt/hexane eluent contained **4a** and the related unsaturated products (4 mg, 4%). The related unsaturated products **3a** contained three isomers, 7-hydroxymethyl-4-undecen-6-one, 7-hydroxymethyl-3-undecen-6-one and 7-hydroxymethyl-2-undecen-6-one in the ratio

of 43 : 31 : 26 ($^1\text{H-NMR}$). 7-Hydroxymethyl-4-undecen-6-one exhibited a complex multiplet between 2.85 and 2.91 ($-\text{COCHBuCH}_2\text{OH}$), a doublet centered at 6.14 ($J = 16.0$ Hz, $-\text{CH}=\text{CHCO}$), and a double triplet at 6.86 ppm ($J = 7.1, 16.0$ Hz, $-\text{CH}_2\text{CH}=\text{CH}$). Only *trans* isomer was observed by $^1\text{H-NMR}$. 7-Hydroxymethyl-3-undecen-6-one showed a doublet at 3.17 ppm ($J = 6.0$ Hz, $-\text{CHCH}_2\text{CO}$), and complex multiplets between 5.25 and 5.50 ($-\text{CH}=\text{CH}$). 7-Hydroxymethyl-2-undecen-6-one displayed a triplet at 2.51 ppm ($-\text{CH}_2\text{CH}_2\text{CO}$), and complex multiplets between 5.25 and 5.50 ($-\text{CH}=\text{CH}$). This mixture of **2a** and **3a** exhibited one large peak and five small peaks (GC), and these peaks were assumed to be **2a** and isomers of **3a**. Catalytic hydrogenation of the mixture of **2a** and **3a** gave pure **2a**: AcOEt (3.0 mL), Pd/C (0.9 mg, 8.4×10^4 mmol) and the mixture of **2a** and **3a** (41.2 mg, 0.206 mmol) were placed in a 50 mL flask under 1 atm of H_2 . The mixture was stirred at room temperature for 3 h. After the resulting catalyst was filtered with suction, the filtrate was concentrated. Pure **2a** was obtained without further purification (40.1 mg, 97%).

The ratio of diol **4a** and the related unsaturated diols was 46:54 ($^1\text{H-NMR}$). Diol **4a** exhibited complex multiplets between 3.63 and 3.91 ($-\text{CH}_2\text{CHOHCH}$ and $-\text{CHCH}_2\text{OH}$). The related unsaturated diols displayed complex multiplets between 3.63 and 3.91 ($-\text{CH}_2\text{CHOHCH}$ and $-\text{CHCH}_2\text{OH}$) and complex multiplets between 5.34 and 5.69 ($-\text{CH}=\text{CH}$). Only 2-butyl-4-octene-1,3-diol displayed a triplet at 4.07 ppm ($J = 7.3$ Hz, $-\text{CHCHOHCH}$). Catalytic hydrogenation of the mixture gave saturated diol **4a** as the sole product: AcOEt (3.0 mL), Pd/C (0.9 mg, 8.4×10^4 mmol) and the mixture (12 mg, 0.059 mmol) were placed in a 50 mL flask under 1 atm of H_2 , and then the reaction mixture was stirred at room temperature for 3 h. After the resulting catalyst was filtered with suction, the filtrate was concentrated. Pure **4a** was obtained without further purification (11.5 mg, 96%) as a 7 : 3 of diastereomer mixtures (GC): $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 0.80-0.90 (m, 6H), 1.17-1.67 (m, 15H), 3.63-3.91 (m, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.0, 14.0, 22.6, 23.0, 24.8, 25.4, 26.0, 28.4, 29.5, 30.0, 31.9, 33.2, 35.6, 44.2, 64.2, 75.6, 75.9; IR (CDCl_3) 3351 cm^{-1} ($\nu_{\text{O-H}}$); EIMS (relative intensity) m/z 187 ($\text{M}^+ - \text{Me}$, 0.9), 131 (9), 95 (22), 84 (53), 69 (47), 55 (100). This product is commercially available and the ^1H - and ^{13}C -NMR spectra are consistent with those of the authentic sample.

1-Triisopropylsiloxy-1-hexene (6). For *cis* isomer: $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 0.87 (t, $J = 7.1$ Hz, 3H), 1.01-1.08 (m, 18H), 1.08-1.20 (m, 3H), 1.28-1.33 (m, 4H), 2.05-2.11 (m, 2H), 4.37 (dt, 1H, $J = 7.3, 6.0$ Hz), 6.24 (dt, 1H, $J = 6.0, 1.4$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 12.0, 14.0, 14.0, 17.7, 17.8, 22.4, 23.3, 31.9, 110.0, 110.0, 138.9, 138.9; IR (CDCl_3) 1655 cm^{-1} ($\nu_{\text{C}=\text{C}}$); For *trans* isomer: $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.00-1.09 (m, 18H), 1.09-1.20 (m, 3H), 1.23-1.31 (m, 4H), 1.83-1.89 (m, 2H), 4.98 (dt, 1H, $J = 11.9, 7.3$ Hz), 6.28 (d, 1H, $J = 11.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 12.0, 13.9, 17.8, 17.8, 22.1, 26.9, 32.7, 111.2, 111.3, 140.4, 140.4.; IR (CDCl_3) 1663 cm^{-1} ($\nu_{\text{C}=\text{C}}$); EIMS (relative intensity) m/z 256 (M^+ , 41), 213 (100), 185 (55), 171 (74), 157 (40), 143 (70), 131 (61), 115 (62), 103 (82), 85 (58), 75 (80), 59 (77); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{32}\text{OSi}$: m/z 256.2222, found: 256.2213.

9-Hydroxymethyl-10-nonadecanone (2i). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 0.87 (t, 6H, $J = 7.1$ Hz), 1.00-1.35 (m, 24H), 1.39-1.49 (m, 1H), 1.49-1.61 (m, 3H), 2.45 (dt, 2H, $J = 3.7, 7.3$ Hz), 2.66 (dq, 1H, $J = 4, 7.3$ Hz), 3.67 (dd, 1H, $J = 4, 11$ Hz), 3.75 (dd, 1H, $J = 7.3, 11$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 14.0, 14.0, 22.6, 22.6, 23.4, 27.4, 28.2, 29.2, 29.2, 29.3, 29.4, 29.7, 31.8, 31.8, 42.8, 53.5, 62.8, 215.4; IR (CDCl_3) 3414 cm^{-1} ($\nu_{\text{O-H}}$), 1708 cm^{-1} ($\nu_{\text{C}=\text{O}}$); EIMS (relative intensity) m/z 312 (M^+ , 0.31), 294 ($\text{M}^+ - \text{H}_2\text{O}$, 9.0), 195 (51), 182 (24), 173 (17), 167 (29), 155 (46), 126 (17), 111 (40), 97 (58), 83 (75), 69 (90), 55 (100); HRMS (EI) (m/z) calcd for $\text{C}_{20}\text{H}_{40}\text{O}_2$: (M^+) 312.3028, found: 312.3036.

Dimer **2i** and unsaturated dimer **3i** were obtained as an inseparable mixture. The $^1\text{H-NMR}$ exhibited complex multiplets between 1.90 and 2.17 ($-\text{CH}_2\text{CH}=\text{CHCH}_2-$) and other complex multiplets from 5.30 to 5.42 ($-\text{CH}_2\text{CH}=\text{CHCH}_2-$). GC analysis of this mixture showed at least six isomers are present. Catalytic hydrogenation of the mixture of **2i** and **3i** gave pure **2i**: AcOEt (3.0 mL), Pd/C (0.9 mg, 8.4×10^4 mmol) and the mixture of **2i** and **3i** (60.4 mg, 0.193 mmol) were placed in a 30 mL flask under 1 atm of H_2 . The mixture was stirred at room temperature for 3 h. After the resulting catalyst was filtered with suction, the filtrate was concentrated. Pure **2i** was obtained without further purification (58.5 mg, 97%).

Reaction of 1i at a Low Concentration. Benzene (60 mL), **1i** (154 mg, 0.987

mmol) and RuHCl(CO)(PPh₃)₃ (47.0 mg, 0.0493 mmol) were placed in a 100 mL two-necked flask equipped with a reflux condenser and a magnetic stirring bar under N₂ atmosphere. The mixture was refluxed with stirring for 1 d. After the solvent was removed, and the residue was purified by column chromatography on silica gel (0%, 2%, 4%, 6%, 8%, 10%, 15% AcOEt/hexane eluent). The 4% AcOEt/hexane eluent contained decanal (**7**) and a mixture of decenals **8** (67.5 mg, 44%) in the ratio of 66:34, which was determined by ¹H-NMR. Decanal (**7**) is commercially available and the ¹H- and ¹³C-NMR spectra are consistent with those of the authentic sample. GC analysis confirmed that the mixture contained *cis*-7-decenal, which is commercially available, corresponded to the retention time of the mixture and ¹H-NMR confirmed that the mixture did not contain 2-decenal. The 8% AcOEt/hexane eluent contained a mixture of **2i**, **3i** and triphenyl phosphine derivatives, which was further purified by preparative HPLC to give **2i** and **3i** (36.6 mg, 23%) as an 83 : 17 mixture.

2-Hydroxymethyl-1,5-diphenyl-3-pentanone (2j). ¹H-NMR (CDCl₃, 500 MHz) δ 2.53-2.62 (m, 1H), 2.69-2.90 (m, 5H) 2.92-2.99 (m, 1H), 3.67-3.75 (m, 2H) 7.07-7.30 (m, 10H); ¹³C-NMR (CDCl₃, 125 MHz) δ 29.3, 34.5, 45.5, 55.6, 62.7, 126.2, 126.6, 128.4, 128.6, 128.7, 128.9, 138.8, 141.0, 213.5; IR (CDCl₃) 3438 cm⁻¹ (ν_{O-H}), 1708 cm⁻¹ (ν_{C=O});

Dimer **2h** and unsaturated dimer **3h** were also obtained as an inseparable mixture. The ¹H-NMR exhibited complex multiplets between 3.26 and 3.32 (-COCHBnCH₂OH), a triplet at 3.82 ppm (*J* = 5.7 Hz, -CHCH₂OH), a doublet centered at 6.71 (*J* = 16.0 Hz, -CH=CHCO) and another doublet at 7.54 ppm (*J* = 16.0 Hz, PhCH=CH).

2-Ethyl-1-hydroxy-3-hexanone (2k). ¹H-NMR (CDCl₃, 500 MHz) δ 0.859 and 0.861 (t, 3H each, *J* = 7.3 Hz), 1.40-1.64 (m, 4H), 2.42 (t, 2H, *J* = 7.1 Hz), 2.57 (qd, 1H, *J* = 7.3, 4.1 Hz), 3.63 (dd, 1H, *J* = 11, 4.1 Hz), 3.72 (dd, 1H, *J* = 11, 7.3 Hz); ¹³C-NMR (CDCl₃, 125 MHz) δ 11.7, 11.7, 13.6, 13.7, 16.7, 21.2, 44.8, 55.0, 55.1, 62.4, 62.4, 62.5, 215.1; R. V. Stevens, K. T. Chapman and H. N. Weller, *J. Org. Chem.*, 1980, **45**, 2030.

References:

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