Supporting Information

"The RuO_4-catalyzed Ketohydroxylation of Olefins"

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General Remarks. Petroleum ether refers to that fraction boiling in the range 35 – 60 °C. Ethyl acetate was purified by distillation over $CaCl_2$ prior to use. $RuCl_3$ was obtained from Aldrich. A stock solution was prepared calculating with $RuCl_3(H_2O)_2$ and dissolving the catalyst (2.44 g, 10 mmol in 100 mL water (0.1 M). The deep brown solution can be stored on the bench for weeks without loss of activity. Flash-chromatography was done on silica 60 (230-400 mesh) using head pressure by means of compressed air. Infrared spectra (IR) were recorded as a thin film between KBr-plates. The instrument used was a Bruker IFS 66 FT-IR spectrophotometer. GC-MS spectra were recorded on a Finnigan Polaris GCQ spectrometer. Proton (^{1}H NMR, 400 MHz) and carbon (^{13}C NMR, 100.6 MHz) nuclear magnetic resonance spectra were recorded in chloroform(d-1) and referenced to the solvent signal. The instrument used was a Bruker DRX 400. All signal points are listed on a δ-scale in ppm.

General Procedure for the Ketohydroxylation. A 100-mL round-bottomed flask equipped with magnetic stirring bar and overpressure valve was charged with $NaHCO_3$ (420 mg, 5 mmol). A 0.1 M aqueous solution of $RuCl_3$ (200 µL, 0.02 mmol) was added and the suspension was diluted with 2 mL H_2O, 12 mL CH_3CN and 12 mL ethyl acetate. Oxone® (6.1 g, 10 mmol) was added in one portion to the resulting brownish suspension (gas evolution!). When the color turned bright yellow the olefin (2 mmol) was added in one portion. The reaction was followed by TLC. After complete conversion the mixture was poured onto 30 mL sat. $NaHCO_3$- and 30 mL sat. Na_2SO_3-solution. Phases were separated and the aqueous layer was extracted with ethyl acetate (3 x 30 mL). After drying the combined organic layer

over Na_2SO_4 and evaporation of the solvent in vacuum the oily crude product was purified by flash-chromatography.

2-Hydroxy-1,2-diphenyl-ethanone (2).[10] White solid. m.p. 137 °C. R_f (pentane / ethyl acetate (3 : 1)). 0.57. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.92 (d, 2*H*), 7.27 – 7.56 (m, 8*H*), 5.92 (s, 1*H*), 4.56 (s, 1*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 200.4, 140.5, 135.4, 130.6, 130.5, 130.3, 130.2, 130.0, 129.2, 77.6. IR (KBr). ν 3379 (br), 2932 (w), 1679 (s), 1206 (m), 1092 (m), 755 (s), 704 (s), 511 (s).

6-Hydroxy-decan-5-one (7).[6g] Colorless oil. R_f (pentane / ethyl acetate (5 : 1)). 0.52. ^{1}H NMR (400 MHz, $CDCl_3$). δ 4.16 (dd, *J* = 5.6, 2.8 Hz, 1*H*), 3.42 (s, 1*H*), 2.45 (m, 2*H*), 1.81 (m, 2*H*), 1.26 – 1.66 (m, 8*H*), 0.91 (m, 6*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 214.0, 77.8, 39.0, 34.9, 28.4, 17.2, 23.9, 15.3. IR (film). ν 3480 (br), 2958 (s), 2873 (m), 1712 (s), 1466 (m), 1045 (m).

1-Hydroxy-octan-2-one (9).[11] Colorless oil. R_f (pentane / ethyl acetate (5 : 1)). 0.36. ^{1}H NMR (400 MHz, $CDCl_3$). δ 4.21 (s, 2*H*), 3.14 (s, 1*H*), 2.37 (t, *J* = 7.6 Hz, 2*H*), 1.61 (m, 2*H*), 1.21 – 1.38 (m, 6*H*), 0.85 (t, *J* = 6.8 Hz, 3*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 210.0, 68.2, 38.5, 31.5, 28.9, 23.8, 22.5, 14.1. IR (film). ν 3426 (br), 2957 (s), 2930 (s), 2859 (s), 1722 (s), 1059 (m).

2-Hydroxy-1-phenyl-ethanone (11).[12] White solid. m.p. 88 °C. R_f (pentane / ethyl acetate (5 : 1)). 0.31. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.92 (d, 2*H*), 7.62 (dd, 1*H*), 7.52 (dd, 2*H*), 4.88 (s, 2*H*), 3.52 (s, 1*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 199.8, 135.8, 134.8, 130.4, 129.2, 66.9. IR (KBr). ν 3430 (s), 3390 (s), 1683 (s), 1236 (m), 688 (m).

2-Hydroxy-1,3-diphenyl-propan-1,3-dione (15).[13] m.p. 110 °C. Yellow solid. R_f (pentane / ethyl acetate (7 : 1)). 0.59. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.99 (d, 4*H*), 7.57 (dd, 2*H*), 7.46 (dd, 4*H*), 6.12 (s, 1*H*), 4.68 (s, 1*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 197.1, 135.8, 135.5, 130.8, 130.3, 79.9. IR (KBr). ν 3448 (br), 3064 (m), 1683 (s), 1597 (m), 1450 (m), 687 (m).

2-Hydroxy-3-oxo-3-phenyl-propionic acid methyl ester (17).[14] Yellow oil. R_f (pentane / ethyl acetate (4 : 1)). 0.43. ^{1}H NMR (400 MHz, $CDCl_3$). δ 8.08 (d, 2*H*), 7.64 (t, 1*H*), 7.51 (t, 2*H*), 5.62 (s, 1*H*), 4.31 (s, 1*H*), 3.72 (s, 3*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 195.1, 170.5, 136.2, 134.4, 131.5, 130.3, 77.8, 54.5. IR (film). ν 3445 (br), 2956 (m), 2856 (s), 1749 (s), 1687 (s), 1449 (m), 1235 (s).

Acetic acid 2-hydroxy-3-oxo-3-phenyl-propyl ester (19).[15] Colorless oil. R_f (pentane / ethyl acetate (3 : 1)). 0.52. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.94 (dd, 2*H*), 7.62 (ddd, 1*H*), 7.49 (dd, 2*H*), 5.28 (dd, *J* = 5.9, 3.2 Hz, 1*H*), 4.53 (dd, *J* = 11.6, 3.2 Hz, 1*H*), 4.09 (dd, *J* = 11.6, 5.9 Hz, 1*H*), 3.93 (s, 1*H*), 1.99 (s, 3*H*). ^{13}C NMR (100 MHz, $CDCl_3$). δ 198.5, 170.9, 134.6, 133.5, 129.2, 128.7, 72.1, 66.9. IR (film). ν 3463 (br), 3064 (w), 2957 (w), 2856 (w), 1742 (s), 1688 (s), 1378 (m), 1235 (s), 1047 (m), 702 (m).