Benzylic Oxidation Catalyzed by Mixed-Valent Dirhodium(II,III) Caprolactamate

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Supporting Information

General. All reagents were commercially obtained unless otherwise noted and were purified according to the guidelines of Armarego and Chai.¹ Yields reported are for isolated yields unless otherwise noted. All products were characterized and in agreement with those previously described. Anhydrous *tert*-butyl hydroperoxide (TBHP) was 6.3 M in decane and was stored over activated 3Å molecular sieves. The preparation of dirhodium(II) caprolactamate [Rh₂(cap)₄·2CH₃CN] has been previously described.² α-Tetralone ethylene acetal (Table 1, entry 1) and 1-indanone ethylene acetal (Table 2, entry 2) were prepared according to the procedure of Gopinath, *et al.*³ Chroman (Table 2, entry 5) was prepared according to the procedure of Hodgetts.⁴ Acetal **8** was prepared according the procedure of Barrett, *et al.*⁵ ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in CDCl₃. Chemical shifts are reported in parts per million (ppm, δ) downfield from Me₄Si (TMS); coupling constants are reported in Hertz (Hz). Preparative chromatographic purification was performed using SiliCycle (60Å, 40-63 mesh) silica gel according to the method of Still.⁶ Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60 F₂₅₄ plates with visualization by fluorescence quenching. Anhydrous CH₂Cl₂ was purified prior to use by nitrogen forced-flow over activated alumina as described.⁷

Representative Procedure (parallel screening): To an oven-dried 1-dram vial equipped with a stirbar was added Rh₂(cap)₄ (0.0027 mmol, 0.01 equiv) and K₂CO₃ (0.139 mmol, 0.50 equiv). The vial was fitted with a rubber septum and empty balloon for oxygen capture. To the mixture

¹ Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; 5th ed., Elsevier Science: New York, 2003.

² Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958.

³ Gopinath, R.; Haque, S. J.; Patel, B. K. *J. Org. Chem.* **2002**, *67*, 5842.

⁴ Hodgetts, K. J., *Tetrahedron Lett.* **2001**, *42*, 3763

⁵ Barrett, A. G. M.; Blaney, F.; Campbell, A. D.; Hamprecht, D.; Meyer, T.; White, A. J. P.; Witty, D.; Williams, D. *J. J. Org. Chem.* **2002**, *67*, 2735.

⁶ Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

⁷ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

was added CH_2Cl_2 , 1,2,3,4-tetrahydronaphthylene (0.272 mmol, 1.0 equiv), and *tert*-butyl hydroperoxide (1.36 mmol, 5.0 equiv). The loss of 1,2,3,4-tetrahydronaphthylene was measured by removing 1 μL aliquots from the solution. The samples were injected on a Hewlett-Packard 5890 gas chromatograph equipped with a SPB-5 column (30 m, 0.25 mm) at 180 $^\circ\text{C}$ (isothermal). Data was obtained via continuous acquisition at 3 minute increments. Retention times: **1** (3.727 min), **3** (4.801 min), **2** (5.060 min).

Representative Procedure (Table 1): A 25-mL flask equipped with a stirbar was charged with substrate (1.09 mmol, 100 mol%), anhydrous DCE (4 mL), NaHCO_3 (0.543 mmol, 50 mol%), and $\text{Rh}_2(\text{cap})_4$ (0.011 mmol, 1.0 mol%). The flask was sealed with a septum allowing inclusion of air. An empty balloon was added to capture oxygen generated during the course of the reaction. To the mixture was added TBHP (5.43 mmol, 5.0 equiv) in one portion via syringe to which the color of the solution immediately turned from light blue to deep red. After stirring for 16 hours, the solution was filtered through a short plug of silica and washed with CH_2Cl_2 . The solvent was evaporated. Preparative column chromatography (SiO_2) yielded the analytically pure compound.

Representative Procedure (Table 2): A 25-mL flask equipped with a stirbar was charged with substrate (1.09 mmol, 100 mol%), anhydrous DCE (4 mL), NaHCO_3 (0.543 mmol, 50 mol%), and $\text{Rh}_2(\text{cap})_4$ (0.006 mmol, 0.5 mol%). The flask was sealed with a septum allowing inclusion of air. An empty balloon was added to capture oxygen generated during the course of the reaction. To the mixture was added TBHP (5.43 mmol, 5.0 equiv) in one portion via syringe to which the color of the solution immediately turned from light blue to deep red. The solution was placed in a preheated oil bath at 40 $^\circ\text{C}$. After 3 hours, additional $\text{Rh}_2(\text{cap})_4$ (0.006 mmol, 0.5 mol%) and TBHP (5.43 mmol, 5.0 equiv) were added. The reaction was stirred for a total of 16 hours at 40 $^\circ\text{C}$ after which time the solution was cooled to room temperature, filtered through a short plug of silica gel, and washed with CH_2Cl_2 . The solvent was evaporated. Preparative column chromatography (SiO_2) yielded the analytically pure compound.

Product Characterization:

Scheme 1, **3**: Data was consistent with the known compound: Tsuji, T.; Okuyama, M.; Ohkita, M.; Kawai, H.; Suzuki, T. *J. Am. Chem. Soc.* **2003**, *125*, 951.

Table 1, entry 8: Data was consistent with the known compound: Morimoto, T.; Fujioka, M.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *Chem. Lett.* **2003**, *32*, 154.

Table 2, entry 6: Data was consistent with the known compound: Joly, S.; Nair, M. S. *Tetrahedron: Asymmetry*, **2001**, *12*, 2283.

Scheme 4, **9**: Data was consistent with the known compound: Barrett, A. G. M.; Blaney, F.; Campbell, A. D.; Hamprecht, D.; Meyer, T.; White, A. J. P.; Witty, D.; Williams, D. J. *J. Org. Chem.* **2002**, *67*, 2735.

Table 2, entry 1: Purified by chromatography on silica gel (4:1 hexanes/EtOAc); clear oil: TLC R_f = 0.34 (3:1 hexanes/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 8.03-8.01 (m, 1H), 7.64-7.57 (comp, 2H), 7.49-7.45 (m, 1H), 4.26-4.13 (comp, 4H), 2.90 (t, J = 6.9 Hz, 2H), 2.35 (t, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 142.8, 133.9, 132.0, 129.2, 126.9, 124.9, 105.7, 65.5, 35.8, 33.5; IR (neat) 1693 (C=O) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$ 204.0786, found 204.0779 (M^+).

Table 2, entry 2: Purified by chromatography on silica gel (4:1 hexanes/EtOAc); clear oil: TLC R_f = 0.32 (3:1 hexanes/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.64 (comp, 3H), 7.58-7.54 (m, 1H), 4.31-4.25 (comp, 2H), 4.17-4.13 (comp, 2H), 2.96 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 151.4, 137.3, 135.4, 130.8, 124.3, 122.7, 100.0, 65.8, 49.1; IR (neat) 1716 ($\text{C}=\text{O}$) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3$ 190.0630, found 190.0633 (M^+).

Table 2, entry 3: Purified by chromatography on silica gel (5:1 hexanes/EtOAc); light yellow oil: TLC R_f = 0.34 (3:1 hexanes/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (dd, J = 1.2, 7.6 Hz, 1H), 7.77 (bs, 1H), 7.60-7.55 (m, 1H), 7.30-7.26 (m, 1H), 4.23 (t, J = 6.4 Hz, 2H), 2.87 (t, J = 6.4 Hz, 2H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.9, 147.9, 146.6, 142.2, 134.4, 127.6, 125.6, 123.5, 86.1, 45.5, 38.8, 27.4; IR (neat) 1731 (C=O), 1693 (C=O) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$ 247.1208, found 247.1217 (M^+).

Table 2, entry 4: Purified by chromatography on silica gel (5:1 hexanes/EtOAc); white solid: TLC R_f = 0.20 (5:1 hexanes/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.52 (comp, 3H), 7.20 (comp, 3H), 4.19 (t, J = 6.4 Hz, 2H), 2.35 (comp, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.6, 144.5, 142.2, 136.7, 134.6, 130.0, 127.6, 126.8, 125.6, 125.5, 124.4, 46.1, 36.4, 21.5; IR (neat) 1683 (C=O) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3\text{S}$ 301.0772, found 301.0769 (M^+).

Scheme 2, **5**: Purified by chromatography on silica gel (3:1 hexanes/EtOAc); yellow solid: TLC R_f = 0.29 (3:1 hexanes/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 2.8 Hz, 1H), 7.21 (dd, J = 8.8, 2.8 Hz, 1H), 3.94 (s, 3H), 3.10-3.01 (comp, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 194.7, 164.2, 137.2, 129.1, 128.8, 121.5, 108.8, 55.8, 37.6, 37.1; IR (neat) 1682 (C=O), 1595 (C=O) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3$ 190.0630, found 190.0625 (M^+).