# Dirhodium(II) Caprolactamate: An Exceptional Catalyst for Allylic Oxidation

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## Supporting Information
(*4 pages*)

**General.** All reagents were commercially obtained unless otherwise noted and were purified according to the guidelines of Armarego and Chai.[1] Olefins were distilled immediately prior to use. Yields reported are for isolated yields unless otherwise noted. All products were fully characterized and in agreement with those previously described.[2] *tert*-Butyl hydroperoxide (TBHP) was purchased from Aldrich as a 5.0-6.0 M solution in decane and stored over activated 3Å molecular sieves. The preparation of dirhodium(II) caprolactamate [$Rh_2(cap)_4 \cdot 2CH_3CN$] has been previously described.[3] $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, $\delta$) downfield from $Me_4Si$ (TMS); coupling constants are reported in Hertz (Hz). UV-Visible spectra were obtained on a Varian Cary 50 spectrophotometer using a xenon flash lamp. Preparative chromatographic purification was performed using SiliCycle (60Å, 40-63 mesh) silica gel according to the method of Still.[4] Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60 $F_{254}$ plates with visualization by fluorescence quenching or aqueous $KMnO_4$ stain. Anhydrous $CH_2Cl_2$ was purified prior to use by nitrogen forced-flow over activated alumina as described.[5]

**Procedure (0.1 mol% catalyst)**: A 25 mL flask equipped with a stirbar was charged with olefin (2.72 mmol, 100 mol%), $CH_2Cl_2$ (10 mL), $K_2CO_3$ (1.36 mmol, 50 mol%), and $Rh_2(cap)_4$ (0.0027 mmol, 0.1 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 (13.6 mmol, 5 equiv) in one portion via syringe to which the color of the solution immediately turned from light blue to deep red. Oxygen generation was observed (filling the balloon). After 1 hour, the solution was filtered through a short plug of silica gel to remove the catalyst. Preparative column chromatography ($SiO_2$) yielded the analytically pure compound.

**Procedure (1.0 mol% catalyst)**:[*] A 5mL flask equipped with a stirbar was charged with olefin (0.272 mmol, 100 mol%), $CH_2Cl_2$ (1 mL), $K_2CO_3$ (0.136 mmol, 50 mol%), and $Rh_2(cap)_4$ (0.00136 mmol, 0.5 mol%). The flask was fitted with a reflux condenser and heated to 40 °C (oil bath) allowing inclusion of air. An empty balloon was added to the condenser to capture oxygen generated during the course of the reaction. To the mixture was added TBHP (1.36 mmol, 5.0 equiv) in one portion via syringe to which the color of the solution immediately turned from light blue to deep red. Oxygen generation was observed (filling the balloon). After 1.5 hours, a second portion of $Rh_2(cap)_4$ (0.00136 mmol, 0.5 mol%) was added followed by a second portion of TBHP (1.36 mmol, 5.0 equiv). After stirring for another 1.5 hours, the solution was filtered through a short plug of silica gel to remove the catalyst. Preparative column chromatography ($SiO_2$) yielded the analytically pure compound.

**Procedure (1 gram preparation of 3-methyl-2-cyclohexene-1-one):** A 100 mL flask equipped with a stirbar was charged with 1-methylcyclohexene (1.00 g, 10.4 mmol, 100 mol%), $CH_2Cl_2$ (40 mL), $K_2CO_3$ (720. mg, 5.20 mmol, 50 mol%), and $Rh_2(cap)_4$ (8.0 mg, 0.01 mmol, 0.1 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 (10.4 mL, 52.0 mmol, 5 equiv) in one portion via syringe to which the color of the solution immediately turned from light blue to deep red. Oxygen generation was observed (filling the balloon). After 20 minutes, the solution was filtered though a short plug of silica gel to remove the catalyst. The solvent was removed via rotary evaporation at 0 °C. Preparative column chromatography ($SiO_2$, 3:1 hexanes/$Et_2O$) yielded 1.02 g (89%) 3-methyl-2-cyclohexene-1-one: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.88 (s, 1H), 2.36-2.27 (m, 4H), 2.03-1.96 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 199.2, 162.4, 126.3, 36.7, 30.6, 24.1, 22.3; IR (KBr) 1670 $cm^{-1}$; TLC $R_f = 0.16$ (3:1 hexanes/$Et_2O$); HRMS (EI) calcd for $C_7H_{10}O$ 110.0732, found 110.0733 (M+).

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

[2] (a) Yu, J.-Q.; Corey, E. J. *Org. Lett.* **2002**, *4*, 2727. (b) Yu, J.-Q.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 3232.

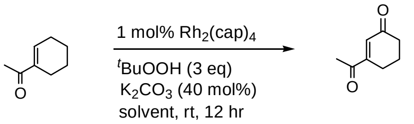
[3] Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958.

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

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

[*] This procedure was followed for the allylic oxidation of 2-cycloheptene-1-one (Table 1, entry 10) and 2-cyclopenten-1-one ethylene ketal (Table 1, entry 11). The allylic oxidation of 1-nitro-cyclohexene (Table 1, entry 5) was conducted using the same procedure but at room temperature for 24 hrs.

***Table 1S***. Yield as a Function of Solvent in the Allylic Oxidation of 1-Acetylcylcohexene Catalyzed by $Rh_2(cap)_4$



| Entry | Solvent[a] | Yield (%) |
|---|---|---|
| 1 | $CHCl_3$ | 41 |
| 2 | $C_6H_6$ | 17 |
| 3 | toluene | 29 |
| 4 | $Et_2O$ | No reaction |
| 5 | THF | No reaction |
| 6 | hexane | 29 |
| 7 | EtOAc | 57 |
| 8 | $CH_3CN$ | No reaction |
| 9 | neat | 34 |
| 10 | $CH_2Cl_2$ | 65 |

[a] Solvent concentration was 0.27 M [substrate] for all entries.

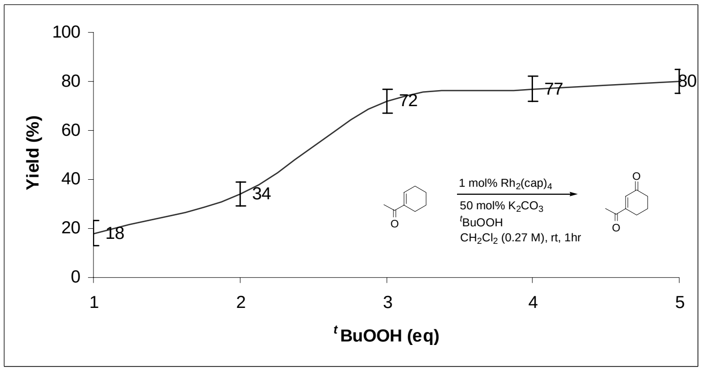


***Figure 1S***. Product Yield as Function of the Equivalents of TBHP for the Allylic Oxidation of 1-Acetylcyclohexene Catalyzed by $Rh_2(cap)_4$

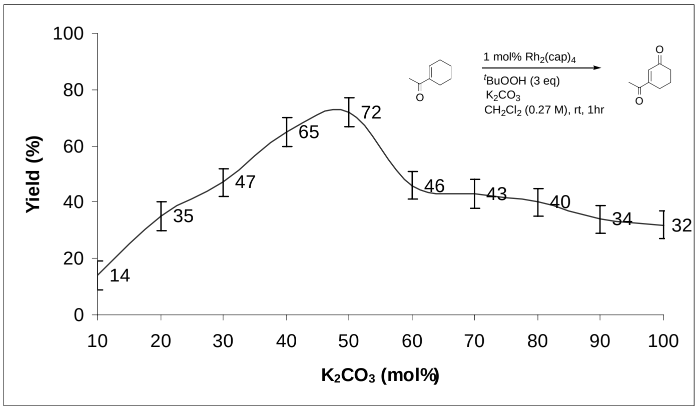


***Figure 2S***. Product Yield as a Function of the Amount of $K_2CO_3$ for the Allylic Oxidation of 1-Acetylcyclohexene Catalyzed by $Rh_2(cap)_4$

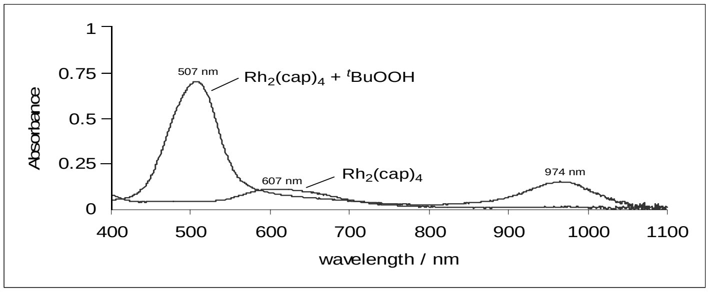
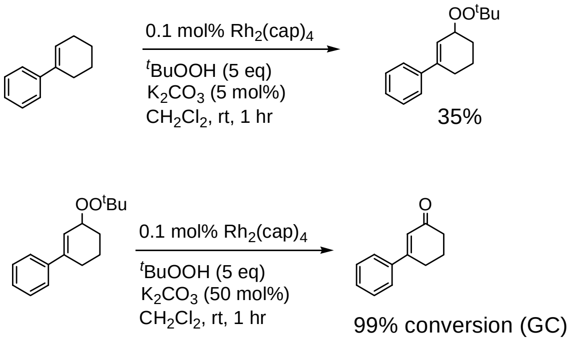
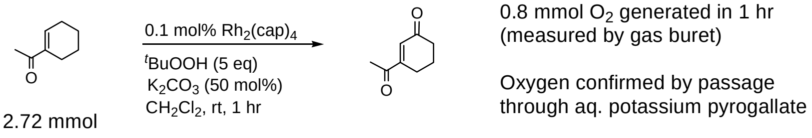


***Figure 3S.*** UV-visible spectrum of $Rh_2(cap)_4$ ($9.05 \times 10^{-4}$ M in $CH_2Cl_2$) upon addition of TBHP

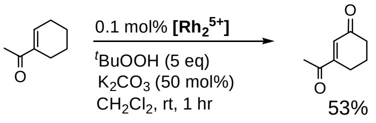
***Scheme 1S***. Evidence for the Intermediacy of *tert*-Butyl Peroxy Ethers in the Allylic Oxidation of 1-Phenylcyclohexene Catalyzed by $Rh_2(cap)_4$



***Scheme 2S***. Measured Oxygen Generation for the Allylic Oxidation of 1-Acetylcyclohexene by $Rh_2(cap)_4$



***Scheme 3S***. Allylic Oxidation of 1-Acetylcyclohexene Catalyzed by $[Rh_2^{5+}]$



**$[Rh_2^{5+}]$**: To a solution of $Rh_2(cap)_4$ (23.0 mg, 0.031 mmol) in $CH_2Cl_2$ (10 mL) open to air was added TBHP (0.625 mL, 3.12 mmol). The solution immediately turned from light blue to deep red (oxygen evolution was observed). After 1 hour, the solution was evaporated to dryness leaving a deep red glass-like solid. Column chromotagraphy ($SiO_2$) using 8:1 DCM/MeOH eluded a red band that was collected and evaporated. The solid was placed under high vacuum (0.1 Torr) for 24 hours. The resultant red solid was submitted to the reaction above yielding the enedione product in 53% yield.