Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 2493–2496

Catalytic asymmetric dihydroxylation of olefins with recyclable osmate-exchanged chloroapatite catalyst

Sanjay K. Dehury* and V. S. Hariharakrishnan*

SMS Pharma Research Center, C-23, Industrial Estate, Sanath Nagar, Hyderabad 500 018, India

Received 5 January 2007; revised 30 January 2007; accepted 8 February 2007
Available online 13 February 2007

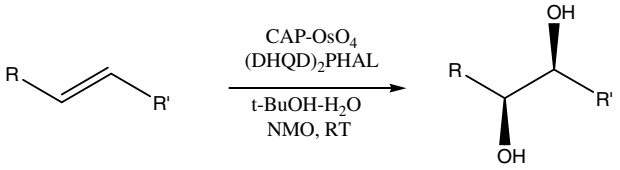
Abstract—An osmate-exchanged chloroapatite (CAP-OsO_4) catalyst was prepared by an ion-exchange technique. CAP-OsO_4 efficiently catalyses asymmetric dihydroxylation of olefins including α,β-unsaturated esters and amides to afford the corresponding diols in high yields and enantioselectivities. The catalyst was reused for several cycles with consistent activity.

Osmium catalyzed asymmetric dihydroxylation of olefins, developed by Sharpless, is a very useful method for the preparation of vicinal diols.[1] In many instances, the chiral diol units are often utilized as key structural constituents of natural products, examples include the synthesis of bicalutamide, diltiazem hydrochloride, and the Taxol C-13 side chain. Nevertheless, the synthetic utility provided by asymmetric dihydroxylation is restricted by the high cost and toxicity due to the contamination of osmium in the product. Kobayashi and co-workers[2] has developed a technique, named microencapsulation, where osmium tetroxide is encapsulated in polymer capsules. Jacobs and co-workers[3] have described immobilization of osmium tetroxide by covalent anchoring and Yao[4] has used the combination of ionic liquids and 4-(dimethylamino)pyridine for dihydroxylation of olefins. Recently, Choudary et al. have not only immobilized osmium tetroxide on layered double hydroxide[5] via ion-exchange but also developed the counterionic stabilization technique[6] for heterogeneization of osmium tetroxide on nanocrystalline MgO by for achiral dihydroxylation.

Recently, there has been research interest on weakly amphoteric apatites as supports, mainly because of the fact that various types of cations and anions can be readily introduced into the framework of apatites due to their large ion-exchange ability and such exchanged apatites are already in use in several organic transformations.[7]

As a result of the above, and in conjunction with our experience on catalytic organic transformations,[8] we believe that osmium tetroxide supported on a biocompatible exchanger such as chloroapatite may function efficiently as a heterogeneous catalyst for asymmetric dihydroxylation. In addition, the basicity provided by chloroapatite may favor the hydrolysis of the osmium–glycolate complex, thus enhancing the turnover frequency of the catalyst. We herein disclose the preparation of an osmate-exchanged chloroapatite (CAP-OsO_4) catalyst and its utility in asymmetric dihydroxylation of olefins (Scheme 1).

In order to generalize the scope of the ion-exchange technique for the heterogeneization of the osmate catalyst through immobilization, chloroapatite and its analogues including fluoroapatite and hydroxyapatite were evaluated for dihydroxylation reactions. In the case of chloroapatite,[9] the Cl^- ions were exchanged with



Yield: 71-96%
ee: 90-97%

Scheme 1.

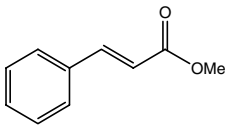
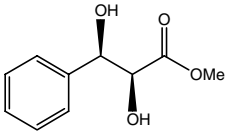
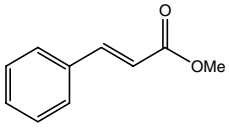
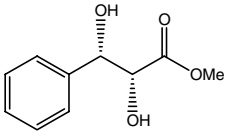
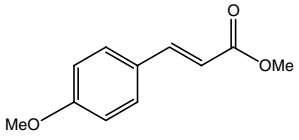
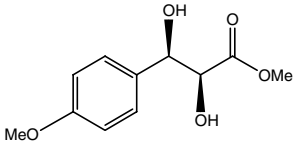
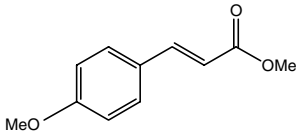
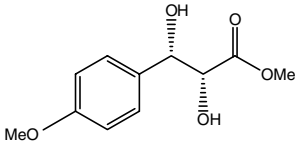
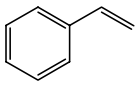
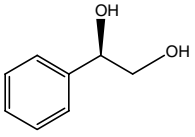
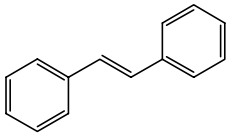
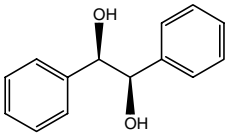
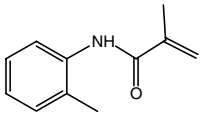
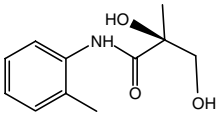
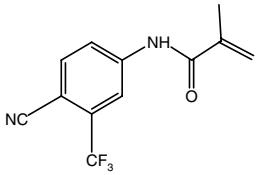
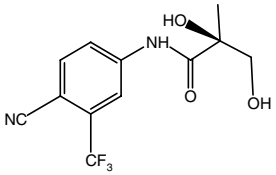
Keywords: Apatite; Asymmetric dihydroxylation; Diols; Osmium tetroxide; α,β-Unsaturated amides.
* Corresponding authors. Tel./fax: +91 40 23814709; e-mail addresses: sanjay@smspharma.com; krishnan@smspharma.com

0040-4039/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2007.02.030

OsO_4^{2-} ions to afford CAP-OsO_4.[10] The osmium content in the CAP-OsO_4 catalyst was 0.786 mmol/g as determined by SEM–EDX and confirmed by quantitative analysis of potassium chloride formed in the exchange process. However, the hydroxyapatite and fluoroapatite analogues of CAP-OsO_4, were obtained with very low osmium content.

In a typical reaction,[11] to a mixture of CAP-OsO_4, $(DHQD)_2PHAL$ and *N*-methylmorpholine-*N*-oxide (NMO) in ^{t}BuOH–water (1:1), an olefin (Table 1, entries 1–8) was added and the reaction was run for the period of time given in the Table. Work-up afforded the corresponding diols in high yields (71–96%) and enantiomeric excess (90–97%). The recovered catalyst and ligand were recycled five times without significant loss of activity and selectivities as presented in Figure 1. Further, to the filtrate, fresh aliquots of substrate and NMO were added and the mixture was stirred for 48 h; however, no product formation was observed. In addition, an iodometry test confirmed the absence of leached osmium.[2b]

Table 1. CAP-OsO_4 catalyzed asymmetric dihydroxylation of olefins

Entry	Substrate	Product	Absol. Config.	Time (h)	Isolated yield (%)	ee[a] (%)
1			2*S*,3*R*	12	93	95
2[b]			2*R*,3*S*	12	92	92
3			2*S*,3*R*	12	89	93
4[b]			2*R*,3*S*	12	87	90
5			*R*	12	96	96
6			*R*,*R*	12	94	97
7[c]			*S*	24	73	90
8[c]			*S*	24	71	92

[a] The ee was determined by HPLC analysis using Diacel Chiralcel OJ column.
[b] Reaction in the presence of $(DHQ)_2PHAL$.
[c] Reaction in the presence of 2.5 mol % of OsO_4, 3 mol % of $(DHQD)_2PHAL$ and 1 mol equiv of $PhSO_2NH_2$ in 1:1 ^{t}BuOH–H_2O.

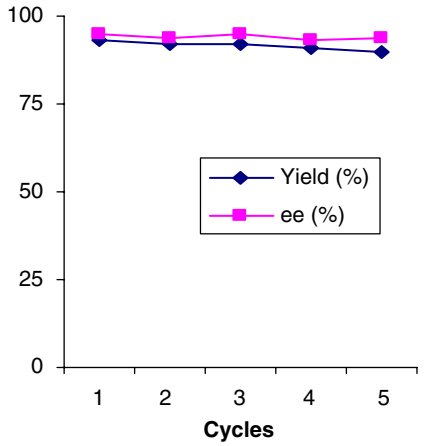


Figure 1. Recycling of the CAP-OsO_4 catalyst for the asymmetric dihydroxylation of methyl cinnamate.

Moreover, various olefins (Table 1, entries 1–6) were successfully screened in asymmetric dihydroxylation reactions using CAP-OsO_4. In some cases, $(DHQ)_2PHAL$ was used as the ligand and the corresponding diols were isolated in high yields and enantiomeric excesses (Table 1, entries 2 and 4).

In order to broaden the synthetic utility of the present process, we studied the asymmetric dihydroxylation of α,β-unsaturated amides. The rate of osmylation of electron deficient olefins such as α,β-unsaturated carbonyls can be very low, while unsaturated esters still give satisfactory reaction rates at room temperature under standard asymmetric dihydroxylation conditions. Unsaturated amides, although more electron rich than the corresponding esters, react sluggishly presumably due to the problems of osmate ester hydrolysis. However, a dramatic increase in the turnover rate could be achieved by increasing the amount of osmate and ligand fivefold in the presence of methane sulfonamide as an additive.[12] Thus, α,β-unsaturated amides (Table 1, entries 7–8) were subjected to CAP-OsO_4 catalyzed asymmetric dihydroxylation. In the absence of any additive, the products were isolated in low yields. On using methane sulfonamide, the reaction did not proceed with much better alacrity. However, increasing the amount of catalyst and ligand threefold and using benzene sulfonamide as an additive were found to be very effective affording the desired products in good yields and high enantiomeric excesses.

In conclusion, CAP-OsO_4 was prepared by a very simple ion-exchange technique using chloroapatite as the support, and was found to be very efficient and reusable for the asymmetric dihydroxylation of a variety of olefins.

Acknowledgment

We gratefully acknowledge Mr. P. Ramesh Babu, CMD, SMS Pharmaceuticals Ltd for unrestricted support.

References and notes

1. (a) Kolbe, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483–2547; (b) Wai, J. S. M.; Marko, I. E.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123–1125; (c) Wang, Z.-M.; Sharpless, K. B. *J. Org. Chem.* **1994**, *59*, 8302–8303; (d) Lu, X.; Xu, Z.; Yang, G. *Org. Process Res. Dev.* **2000**, *4*, 575–576.
2. (a) Nagayama, S.; Endo, M.; Kobayashi, S. *J. Org. Chem.* **1998**, *63*, 6094–6095; (b) Kobayashi, S.; Endo, M.; Nagayama, S. *J. Am. Chem. Soc.* **1999**, *121*, 11229–11230; (c) Kobayashi, S.; Ishida, T.; Akiyama, R. *Org. Lett.* **2001**, *3*, 2649–2652; (d) Ishida, T.; Akiyama, R.; Kobayashi, S. *Adv. Synth. Catal.* **2003**, *345*, 576–579.
3. Severeyns, A.; De Vos, D. E.; Fiermans, L.; Verpoort, F.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 586–589.
4. Yao, Q. *Org. Lett.* **2002**, *4*, 2197–2200.
5. (a) Choudary, B. M.; Chowdari, N. S.; Jyothi, K.; Kantam, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 5341–5345; (b) Choudary, B. M.; Chowdari, N. S.; Kantam, M. L.; Raghavan, K. V. *J. Am. Chem. Soc.* **2001**, *123*, 9220–9221; (c) Choudary, B. M.; Chowdari, N. S.; Madhi, S.; Kantam, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4620–4623.
6. (a) Choudary, B. M.; Jyothi, K.; Kantam, M. L.; Sreedhar, B. *Adv. Synth. Catal.* **2004**, *346*, 45–48; (b) Choudary, B. M.; Jyothi, K.; Roy, M.; Kantam, M. L.; Sreedhar, B. *Adv. Synth. Catal.* **2004**, *346*, 1471–1480.
7. (a) Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, *122*, 7144–7145; (b) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124*, 11572–11573; (c) Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2003**, *125*, 11460–11461; (d) Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 10657–10666.
8. (a) Chaudhuri, M. K.; Dehury, S. K.; Hussain, S. *Tetrahedron Lett.* **2005**, *46*, 6247–6251; (b) Kantam, M. L.; Haritha, Y.; Neeraja, V.; Kavita, V. B.; Chaudhuri, M. K.; Dehury, S. K. *Adv. Synth. Catal.* **2005**, *347*, 641–645; (c) Chaudhuri, M. K.; Dehury, S. K.; Duarah, A.; Gogoi, N. M.; Hussain, S.; Kantam, M. L. *Adv. Synth. Catal.* **2005**, *347*, 1349–1352.
9. *Preparation of chloroapatite*: $Ca(NO_3)_2{\cdot}4H_2O$ (15.576 g, 0.066 mol) dissolved in water (60 mL) was brought to pH 11–12 with concentrated NH_4OH and then diluted to 120 mL with water. A solution of $(NH_4)_2HPO_4$ (5.28 g, 0.04 mol) and NH_4Cl (0.713 g, 0.013) in 100 mL of water was brought to pH 11–12 with concentrated NH_4OH and thereafter diluted to 160 mL with water. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was added dropwise over a period of 30 min to produce a milky, somewhat gelatinous precipitate, which was then stirred and boiled for 10 min. The precipitate was filtered, washed, dried at 80 °C overnight, and calcined at 500 °C for 3 h. All the synthetic steps were carried out using doubly distilled water.
10. *Preparation of CAP-OsO_4 catalyst*: 1.5 g of chloroapatite was suspended in 150 mL of 1.87 mmol (0.689 g) aqueous potassium osmate solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water and vacuum dried to obtain 1.916 g of CAP-OsO_4 (0.786 mmol of Os per g as determined by SEM–EDX).
11. *Procedure for asymmetric dihydroxylation of methyl cinnamate*: CAP-OsO_4 (100.2 mg, 0.08 mmol), $(DHQD)_2PHAL$ (78.0 mg, 0.1 mmol), and *N*-methylmorpholine-*N*-oxide

(NMO, 15.0 mmol) were taken in a round bottomed flask containing ^{t}BuOH–water (1:1, 60 mL) and stirred at room temperature. To this mixture was added methyl cinnamate (1.62 g, 10 mmol) slowly over 12 h. After completion of the reaction, the CAP-OsO_4 catalyst was filtered and washed with methanol. Ethyl acetate and 1 N HCl were added to the combined filtrates. After removing the solvent, the crude material was chromatographed on silica gel with EtOAc–hexanes to afford the corresponding *cis*-diol. Yield: 1.82 g (93%); ee: 95%; $[\alpha]_D^{25}$ −10.60 (*c* 1.0 $CHCl_3$) [lit.[13] −10.7 (*c* 1.0, $CHCl_3$)]; ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 3.32 (br s, 2H), 3.81 (s, 3H), 4.36 (d, $J = 2.8$ Hz, 1H) 5.01 (d, $J = 2.8$ Hz, 1H), 7.36 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 52.8, 74.4, 74.7, 126.2, 128.1, 128.4, 139.9, 173.1; HPLC (Daicel Chiralcel OJ, 10% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 19.1$ (minor), $t_R = 26.7$ (major). The chiral ligand was recovered from the aqueous layer.

12. Bennani, Y. L.; Sharpless, K. B. *Tetrahedron Lett.* **1993**, *34*, 2079–2082.
13. Denis, J. N.; Correa, A.; Greene, A. E. *J. Org. Chem.* **1990**, *55*, 1957–1959.