

Catalytic Asymmetric Dihydroxylation of Aliphatic Olefins with Reusable Resin-Osmium Tetroxide

Boyapati M. Choudary,* Karangula Jyothi, Sateesh Madhi, M. Lakshmi Kantam

Indian Institute of Chemical Technology, Hyderabad – 500 007, India
 Fax: (+91)-40-27160921; e-mail: choudary@iict.res.in, bmchoudary@yahoo.com

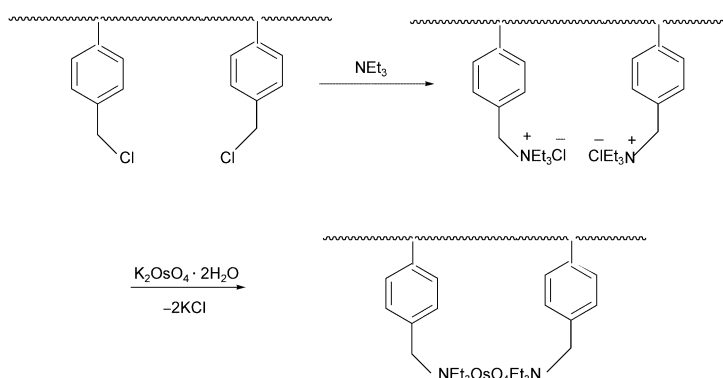
Received: June 25, 2003; Accepted: September 5, 2003

Abstract: Asymmetric dihydroxylation of aliphatic olefins to chiral diols with good yields and ees by a heterogeneous Resin-OsO₄ catalyst using ferricyanide as cooxidant is disclosed for the first time. The catalyst was recovered quantitatively by simple filtration and reused for several times without significant loss of activity.

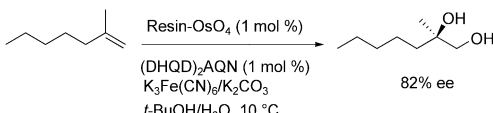
Keywords: aliphatic olefins; asymmetric dihydroxylation; chiral diols; immobilization; supported catalysts; resin-osmium tetroxide

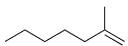
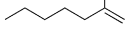


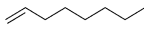
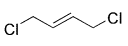
Osmium-catalyzed asymmetric dihydroxylation (AD) is an efficient method for the transformation of unfunctionalized olefins to chiral diols.^[1] Aliphatic olefins, especially terminal ones provide the most useful chiral diols in AD reaction.^[2] Various cooxidants such as *N*-methylmorpholine *N*-oxide (NMO), potassium ferricyanide [K₃Fe(CN)₆] and very recently molecular oxygen^[3] are effectively used to facilitate the Os(VI)/Os(VIII) catalytic cycle that allows the use of catalytic amounts of osmium tetroxide in the dihydroxylation reaction. K₃Fe(CN)₆ is found to be an efficient oxidant to afford high yields and ees in the homogeneous AD reactions of aliphatic olefins. Although the AD reac-

tions catalyzed by OsO₄ could be applied to the synthesis of pharmaceuticals, fine chemicals, etc., the high cost, and possible contamination of toxic osmium in the product restricts its use in industry. To overcome the above problems, heterogenization of the ligands on a polymer or silica gel support and eventual complexation with osmium, a possible solution to address this issue attempted by several groups, failed to recover and reuse the osmium since the coordination of anchored ligands and osmium tetroxide is in equilibrium.^[4–6] When microencapsulated (MC) polymer-supported osmium catalysts are employed in AD of aliphatic olefins using NMO as cooxidant,^[7] moderate ees are obtained. On the other hand, a lower yield is reported in the AD of 5-decene despite slow addition of ferricyanide.^[8] Therefore, we felt that there is a strong need to develop a robust heterogeneous catalytic system to withstand the vagaries of the reaction conditions induced by various cooxidants for the AD of aliphatic olefins. Recently, we designed and developed an ion-exchange technique for a recoverable and reusable osmium catalyst immobilized on layered double hydroxides (LDH-OsO₄) and quaternary ammonium salts covalently bound to resin (Resin-OsO₄) (Scheme 1) for the AD of aromatic olefins using various cooxidants.^[9] In view of the importance of aliphatic terminal chiral diols and the necessity to have a recyclable heterogenized OsO₄ catalyst, we undertook studies on the AD of aliphatic olefins.^[3] We herein report the AD of aliphatic olefins



Scheme 1. Schematic representation of Resin-OsO₄ catalyst preparation.

Table 1. Asymmetric dihydroxylation of olefins with Resin-OsO₄


Entry	Olefin	Yield [%]	ee [%] ^[a]	Diol config. ^[b]
1		85	82 (86) ^[c]	<i>R</i>
2 ^[b]		83	80	<i>R</i>
3	H ₁₇ C ₆ 	80	74	<i>R</i>
4		80	70 ^[e]	<i>R</i>
5		85	84	<i>R</i>
6 ^[f]		90	75 ^[e]	<i>S, S</i>

^[a] The ee is determined by HPLC analysis.

^[b] The absolute configuration was determined by comparison of specific rotation with literature value.

^[c] ee with 3 mol % ligand.

^[d] Results after 5th cycle.

^[e] Determined by comparison of specific rotation with literature value.

^[f] 1 mmol of CH₃SO₂NH₂ was added.

affording good ees and yields using a heterogeneous resin-OsO₄ with 1,4-bis(dihydroquininyl)-anthraquinone [(DHQD)₂AQN] ligand for the first time.

We performed AD of various aliphatic olefins by taking an olefin (1 mmol), resin-OsO₄ (1 mol %), (DHQD)₂AQN (1 mol %), K₃Fe(CN)₆, and K₂CO₃ (3.0 equivs.) in *t*-BuOH-H₂O system (1:1, 10 mL) at 10 °C. All the olefins investigated gave good yields ranging from 80–90% and ees (Table 1). When the reaction is conducted with the (DHQD)₂PHAL ligand under similar reaction conditions, a lower ee is observed. Higher concentrations of the ligand (3 mol %), did show a small improvement in ees (4%), Table 1, entry 1.

The Resin-OsO₄ was recovered quantitatively by simple filtration. The recovered catalyst along with the replenished chiral ligand (to make up 1 mol %) was reused and a marginal decrease in activity was noticed during 5th–7th cycles (Table 2). When the reaction was conducted with the filtrate obtained by treatment of the catalyst in a solvent system for prolonged time no product formation was observed. The absence of osmium in the filtrate is further reconfirmed using the iodometry test.^[7b]

In conclusion, we have successfully applied the heterogeneous Resin-OsO₄ catalyst for the AD of aliphatic olefins affording chiral diols without slow addition of cooxidant for the first time with good yields and ees, having consistency for five cycles. The catalyst is

Table 2. Reuse of Resin-OsO₄ catalyst in the AD of 2-methyl-1-heptene.

Run	Time [h]	Yield [%]
1	12	85
2	12	84
3	12	83
4	12	84
5	12	83
6	12	80
7	12	78
8	24	35

easily recovered from reaction mixture by simple filtration after completion of the reaction. The high binding ability of the heterogeneous osmium catalyst enables the use of an equimolar ratio of ligand to osmium to give good enantioselectives in asymmetric dihydroxylation of aliphatic olefins.

Experimental Section

Preparation of the Resin-OsO₄ Catalyst

Modified resin was obtained by quaternization of triethylamine (2.1 mL, 21 mmol) with 1 g of chloromethylated styrene-divinylbenzene copolymer (Merrifield resin, capacity ~2.1 mequiv/g) in chloroform (20 mL) under reflux for 24 h. 1 g of quaternary ammonium resin was suspended in 100 mL of 0.8 mmol aqueous potassium osmate solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 300 mL of water and vacuum dried to obtain the resin-OsO₄ (0.641 mmol of Os per g, 12.19%) as determined by scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX). This result was revalidated by quantitative estimation of the potassium halide formed in the ion-exchange process using 0.1 N silver nitrate solution as titrant in the presence of potassium chromate.

Typical Procedure for Asymmetric Dihydroxylation of Aliphatic Olefins with Resin-OsO₄ using K₃Fe(CN)₆ as the Cooxidant

Resin-OsO₄ (15.6 mg, 1 mol %), (DHQD)₂AQN (8.6 mg, 1 mol %), K₃Fe(CN)₆ (990 mg, 3.0 equivs.) and K₂CO₃ (420 mg, 3 equivs.) and *t*-BuOH-H₂O (1:1, 10 mL) were placed in a round-bottomed flask and stirred at room temperature for 5 min. For 1,2-disubstituted and trisubstituted olefins CH₃SO₂NH₂ (95 mg, 1 mmol) was added. The solution was cooled to 10 °C and then an olefin was added. The reaction mixture was stirred at 10 °C for 12–15 h, and then to this Na₂SO₃ (0.8 g) was added and the suspension was brought up to room temperature with vigorous stirring. Resin-OsO₄ catalyst was filtered and washed with ethyl acetate. The aqueous layer was further extracted with ethyl acetate. The combined organic

layers were washed with 2 M aqueous NaOH solution, if $\text{CH}_3\text{SO}_2\text{NH}_2$ was used. After removing the solvent, the crude material was chromatographed on silica gel with EtOAc/hexane to afford the corresponding *cis*-diol. The ee values of the derivatized diols were determined by HPLC analysis using Chiralcel OD-H column.

Acknowledgements

K. Jyothi thanks the Indian Institute of Chemical Technology, India for the award of a research fellowship and S. M. thanks the Council of Scientific and Industrial Research, India for the award of a senior research fellowship.

References and Notes

- [1] a) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483–2547; b) I. E. Marko, J. S. Svendsen, in *Comprehensive Asymmetric Catalysis* Vol. II, (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, pp. 723–787; c) K. Bergstad, S. Y. Jonsson, J.-E. Backvall, *J. Am. Chem. Soc.* **1999**, *121*, 10424–10425; d) J. S. M. Wai, I. E. Marko, J. S. Svendsen, M. G. Finn, E. N. Jacobsen, K. B. Sharpless, *J. Am. Chem. Soc.* **1989**, *111*, 1123–1125; e) A. Severeys, D. E. De Vos, L. Fireman, F. Verpoort, P. J. Grobet, P. A. Jacobs, *Angew. Chem. Int. Ed.* **2001**, *40*, 586–589.
- [2] H. Becker, K. B. Sharpless, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 448–451.
- [3] a) C. Dobler, G. Mehlretter, M. Beller, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3026–3028; b) C. Dobler, G. M. Mehlretter, U. Sundermeier, M. Beller, *J. Am. Chem. Soc.* **2000**, *122*, 10289–10297.
- [4] Review: a) C. Bolm, A. Gerlach, *Eur. J. Org. Chem.* **1998**, *1*, 21–27; b) P. Salvadori, D. Pini, A. Petri, *Synlett* **1999**, 1181–1190.
- [5] For polymer supported chiral ligands see: a) B. M. Kim, K. B. Sharpless, *Tetrahedron Lett.* **1990**, *31*, 3003–3006; b) D. Pini, A. Petri, A. Nardi, C. Rosini, P. Salvadori, *Tetrahedron Lett.* **1991**, *32*, 5175–5178; c) H. Han, K. D. Janda, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1731–1733.
- [6] For achiral ligand-osmium tetroxide, see: a) G. Cainelli, M. Contento, F. Manescalchi, L. Plessi, *Synthesis* **1989**, 45–46; b) W. A. Herrmann, R. M. Kratzer, J. Blümel, H. B. Friedrich, R. W. Fischer, D. C. Apperley, J. Mink, O. Berkesi, *J. Mol. Catal.* **1997**, *120*, 197–205.
- [7] For microencapsulated osmium tetroxide, see: a) S. Nagayama, M. Endo, S. Kobayashi, *J. Org. Chem.* **1998**, *63*, 6094–6095; b) S. Kobayashi, M. Endo, S. Nagayama, *J. Am. Chem. Soc.* **1999**, *121*, 11229–11230; c) T. Ishida, R. Akiyama, S. Kobayashi, *Adv. Synth. Catal.* **2003**, *345*, 576–579.
- [8] S. Kobayashi, T. Ishida, R. Akiyama, *Org. Lett.* **2001**, *3*, 2649–2652.
- [9] a) B. M. Choudary, N. S. Chowdari, M. L. Kantam, K. V. Raghavan, *J. Am. Chem. Soc.* **2001**, *123*, 9220–9221; b) B. M. Choudary, N. S. Chowdari, K. Jyothi, M. L. Kantam, *J. Am. Chem. Soc.* **2002**, *124*, 5341–5345.