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# $OsO_4$ in Ionic Liquid $[Bmim]PF_6$: A Recyclable and Reusable Catalyst System for Olefin Dihydroxylation. Remarkable Effect of DMAP

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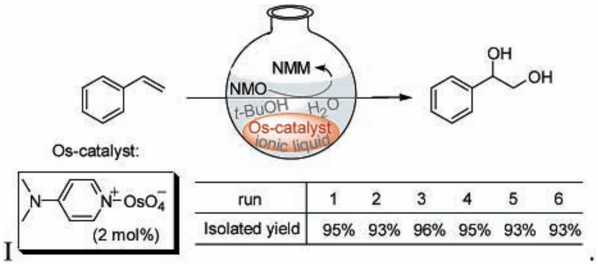
## ABSTRACT



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| run | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Isolated yield | 95% | 93% | 96% | 95% | 93% | 93% |

**The combination of the ionic liquid $[bmim]PF_6$ and DMAP provides a most simple and practical approach to the immobilization of $OsO_4$ as catalyst for olefin dihydroxylation. Both the catalyst and the ionic liquid can be repeatedly recycled and reused in the dihydroxylation of a variety of olefins with only a very slight drop in catalyst activity.**

Development of cost-effective and environmentally benign catalytic systems is one of the main themes of contemporary synthetic chemistry. From the viewpoints of atom economy[1] and green chemistry,[2] a highly desirable catalytic process should be one that involves low catalyst input and minimal production of byproducts and hazardous solvent wastes with maximum product output. In this context, efficient recycling and subsequent reuse of an otherwise more efficient homogeneous catalyst may provide a powerful alternative to a generally less efficient but operationally and economically more advantageous heterogeneous catalyst.[3] We report herein a unique catalyst−solvent combination system that uses a room-temperature ionic liquid as the key solvent component for the anchoring of an osmium catalyst for olefin dihydroxylation. This allows the dihydroxylation reaction to be performed under standard homogeneous conditions while both the catalyst and the anchoring solvent can be repeatedly recycled and reused.

Osmium-catalyzed olefin dihydroxylation, represented by the well-known Upjohn procedure[4] for the production of vicinal diols and its asymmetric version developed by Sharpless et al.,[5] is one of the most useful transformations for the functionalization of alkenes. Although these reactions

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(1) Trost, B. M. *Angew. Chem.* **1995**, *107*, 285−307; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281.

(2) For leading reviews and monographs on green chemistry, see: (a) *Green Chemistry: Designing Chemistry for the Environment. ACS Symposium Series No. 626*; Anastas, P. T., Williamson, T. C., Eds.; American Chemical Society: Washington, DC, 1996. (b) Anastas, P. T.; Warner, J. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998. (c) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*; Anastas, P. T., Williamson, T. C., Eds.; Oxford University Press: New York, 1999.

(3) For general discussions on homogeneous catalysts and their heterogenization, see: (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornil, B., Hermann, W. A., Eds.; Wiley-VCH: Weiheim, 1996; Chapter 3.1. (b) *Chiral Catalyst Immobilization and Recycling*; De Vos, D. E., Vankelecom, I. F. J., Jacobs, P. A., Eds.; VCH: Weiheim, 2000.

(4) (a) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973−1976. For an early review, see: (b) Schröder, M. *Chem. Rev.* **1980**, *80*, 7.

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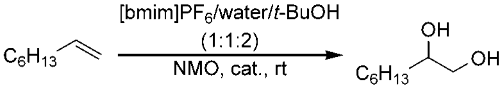
have found widespread application in organic synthesis, the high cost of the osmium catalyst as well as the ligand in the case of asymmetric dihydroxylation (AD), coupled with the hazardous toxicity and volatility of $OsO_4$,[6] obstructs their large-sale industrial application.[7] Early attempts to immobilize $OsO_4$ on polymeric supported tertiary amines[8,9] failed to recover and reuse the catalyst due to osmium leaching and catalyst decomposition. Kobayashi has previously reported[10] that $OsO_4$ could be microencapsulated in a polymer matrix and used as a recyclable and reusable catalyst for olefin dihydroxylation. However, high loading of osmium was required in a typical dihydroxylation reaction. Very recently, two conceptually new approaches to the immobilization of osmium catalyst have been achieved on the basis of the formation of a hydrolytically stable osmium monoglycolate derived from a silica-bound tetrasubstituted olefin[11] and by using an ion-exchange technique[12] on various solid supports.

In searching for a more practical and efficient approach to the immobilization of the osmium catalyst, we were attracted by the unique properties of room-temperature ionic liquids[13] that have recently emerged as environmentally benign reaction media as well as new vehicles for the immobilization of transition metal-based catalysts. Using 1-octene as a test substrate, we set out to examine the osmium-catalyzed dihydroxylation under the standard Upjohn conditions[4] ($OsO_4$/NMO in *t*-BuOH/$H_2O$) in the presence of the room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] $PF_6$) (Table 1).[14] After 16h at room temperature, all the volatiles were removed under reduced pressure and the product extracted from the ionic liquid layer by ether. Standard chromatographic purification gave the pure diol product in 96% yield (Table 1, entry 1, run 1). A second run of the reaction was then conducted using the recovered ionic liquid with a new batch of the olefin under otherwise identical conditions. It is noteworthy that the diol was isolated in 90% yield (Table 1, entry 1, run 2) even without any replenishment of the catalyst, indicating that both the ionic liquid and the catalyst were recyclable and reusable. However, further recycling and reuse of the catalyst system resulted in a dramatic decrease in the yield of the product (Table 1, entry 1, runs 3 and 4). This suggested that the active catalytic species, either $OsO_4$ itself or complex **1** (Figure 1), formed in situ during the course of the reaction, underwent significant leaching after each recycling and reuse. Since complex formation between $OsO_4$ and an amine ligand is expected to be reversible, it is reasonable to assume that a stronger binding and more polar amine might help in preventing complex dissociation and enhance its partitioning in the more polar ionic liquid layer. This reasoning was then tested with 4-(dimethylamino)-pyridine (DMAP), with the anticipation that complex **2**[15] would be more resistant to osmium leaching. To our delight,

**Table 1.** Effect of DMAP on $OsO_4$-Catalyzed Dihydroxylation of 1-Octene in Ionic Liquid[a]



| entry | cat. (quantity) | yield[b] (%) | | | |
|---|---|---|---|---|---|
| | | run 1 | run 2 | run 3 | run 4 |
| 1 | OsO4(2 mol%) | 96 | 90 | 62 | 36 |
| 2 | OsO4(2 mol%) + DMAP (2.4 mol%) | 99 | 94 | 97 | 93 |

[a] All reactions were performed with 2 mmol of 1-octene, 1.1−1.2 equiv of NMO in the following solvent system: [bmim]$PF_6$ (1 mL), $H_2O$ (1 mL), and *t*-BuOH (2 mL) at room temperature for 16 h. [b] Isolated yield. [bmim]$PF_6$ = 1-butyl-3-methylimidazolium hexafluorophosphate.

1 2

**Figure 1.** Formation of Complexes between $OsO_4$ and Amine Ligands. **1**: NMM·$OsO_4$. **2**: DMAP·$OsO_4$.

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(5) (a) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968−1970. For selected reviews on Sharpless asymmetric dihydroxylation, see: (b) Kolb, H. C.; Van Niewenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547. (c) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; VCH: Weinheim, 2001; pp 357−398.

(6) Even when other forms of osmium such as $OsCl_3$ and $K_2[OsO_2(OH)_4]$ are used, volatile-free $OsO_4$ is present in some stage of the catalytic cycle.

(7) For a case study, see: Ahrgren, L.; Sdutin, L. *Org. Proc. Res. Dev.* **1997**, *1*, 425−427.

(8) Cainelli, G.; Contento, M.; Manescalchi, F.; Plessi; L. *Synthesis* **1989**, 45−47.

(9) Herrmann, W. A.; Kratzer, R. M.; Blümel, J.; Friedrich, H. B.; Fischer, R. W.; Apperley, D. C.; Mink, J.; Berkesi, O. *J. Mol. Catal., A* **1997**, *120*, 197−205.

(10) (a) Nagayama, S.; Endo, M.; Kobayashi, S. *J. Org. Chem.* 1**998**, *63*, 6094−6095. (b) Kobayashi, S.; Endo, M.; Nagayama, S. *J. Am. Chem. Soc.* **1999**, *121*, 11229−11230. (c) Kobayashi, S.; Ishida, T.; Akiyama, A. *Org. Lett.* **2001**, *3*, 2649−2652.

(11) Severeyns, A.; De Vos, D. E.; Fiermans, L.; Verpoort, F.; Grobert, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 586−589.

(12) (a) Choudary, B. M.; Chowdari, N. S.; Kantam, M. L.; Raghavan, K. V. J. *Am. Chem. Soc.* **2001**, *123*, 9220−9221. (b) Choudary, B. M.; Chowdari, N. S.; Madhi, S.; Kantam, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4620−4623. Choudary, B. M.; Chowdari, N. S.; Jyothi, K.; Kumar, N. S.; Kantam, M. L. *Chem. Commun.* **2002**, 586−587. (c) (d) Choudary, B. M.; Chowdari, N. S.; Jyothi, K.; Kantam, M. L.; *J. Am. Chem. Soc.* **2002**, *124*, 5341−5349.

(13) For recent reviews on ionic liquids and their application as innovative solvents in transition metal-catalyzed reactions, see: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789. (c) Sheldon, R. *Chem. Commun.* **2001**, 2399−2407.

(14) Although [bmim]$PF_6$ is essentially immiscible with either solvent, a completely homogeneous mixture was formed upon addition of NMO and the olefin under these conditions.

(15) An NMR experiment established that upon mixing equimolar amounts of $OsO_4$ and DMAP in $CDCl_3$, a deep orange-red complex was immediately formed:

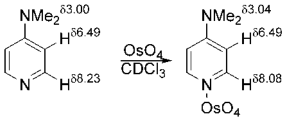
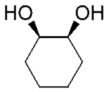
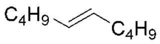
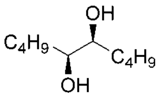
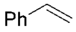
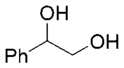
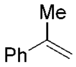
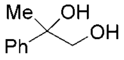
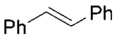
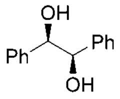
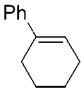
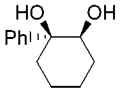


**Table 2.** *cis*-Dihydroxylation of Olefins in Ionic Liquid Using $OsO_4$−DMAP as Recyclable and Reusable Catalyst[a]

| entry | olefin | conditions | product | yield[b] | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | run 1 | run 2 | run 3 | run 4 | run 5 | run 6 |
| 1 |  | rt, 16h |  | 93% | 89% | 91% | 87% | 85% | 82% |
| 2 |  | rt, 24h |  | 93% | 87% | 89% | 80% | 93%[c] | |
| 3 |  | rt, 16h |  | 95% | 93% | 96% | 95% | 93% | 93% |
| 4 |  | rt, 16h |  | 99% | 95% | 98% | 97% | 90% | 95% |
| 5 |  | rt, 24h |  | 73% | 77% | 80% | 79% | 77% | 78% |
| 6 |  | 50 °C, 6h |  | 87% | 76% | 86% | 84% | 80% | 77% |

[a] For general reaction conditions, see footnote a, Table 1. [b] Isolated yield. [c] The reaction was run for 40 h.

the use of 1.2 equiv of DMAP relative to $OsO_4$ resulted in a drastic improvement in the recyclability of the catalyst, giving a consistently high yield of the product even after four consecutive runs (Table 1, entry 2).

The efficiency of this new protocol for the immobilization of $OsO_4$ was further examined with a variety of other substrates, including mono-, di-, and trisubstituted aliphatic, as well as aromatic, olefins (Table 2). In almost all the cases tested, the dihydroxylation went smoothly at room temperature with 2 mol % catalyst, giving a high yield of the products over at least five consecutive runs of recycling and reuse and with only a very slight drop in catalyst activity. In the case of a sterically unfavorable substrate (Table 2, entry 6), a moderately elevated temperature was required to afford the product in high yield.

In summary, this work demonstrates that the combination of an ionic liquid and DMAP provides a most simple and practical[16] approach to the immobilization of osmium catalyst for olefin dihydroxylation. Further optimization of the recyclability of the catalyst as well as extension to the use of chiral ligands[5] for asymmetric olefin dihydroxylation is currently underway in our laboratory.

**Acknowledgment.** This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, and by Northern Illinois University.

**Supporting Information Available:** Experimental procedures and NMR data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) $[Bmim]PF_6$ can either be purchased from Acros Organics at relatively low cost or readily made in large quantities by simple procedures.