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OsO_4-catalyzed dihydroxylation of olefins in ionic liquid $[emim]BF_4$: a recoverable and reusable osmium

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Abstract—We have demonstrated the usefulness of recoverable and reusable immobilized OsO_4 in $[emim]BF_4$ for dihydroxylation of several olefins. This approach is simple and practical. It should be noted that the volatility and toxicity of OsO_4 are greatly suppressed when the ionic liquid $[emim]BF_4$ is used. © 2002 Elsevier Science Ltd. All rights reserved.

Ionic liquids have several interesting properties.[1] They can dissolve a wide range of organometallic compounds and are miscible with organic compounds. They are highly polar but non-coordinating. They exhibit excellent chemical and thermal stabilities with ease of reuse. They are immiscible with a wide range of organic solvents. It is possible to vary their miscibility with water only by changing the counter anion. They have essentially negligible vapor pressure. On the other hand, osmium-catalyzed oxidation reaction is one of the most useful methods for dihydroxylation of olefins to give the corresponding diols.[2] This oxidation proceeds in the presence of a catalytic amount of OsO_4 with a cooxidant such as *N*-methylmorpholine *N*-oxide (Upjohn procedure),[3] potassium ferricyanide, hydrogen peroxide, molecular oxygen[4] or hydrogen peroxide-flavin base.[5] Although these reactions have had widespread applications in organic synthesis, there have been few large-scale industrial applications due to toxicity, high cost performance, and volatility of the reagent. To overcome these problems, several immobilized osmium catalysts have been developed. Kobayashi reported microencapsulated OsO_4 and ABS (acryronitrile-butadiene-polystyrene) polymer-supported OsO_4.[6] Recently, new approaches using various solid supports in order to recovery and reuse OsO_4 have been reported.[7] However, there is still a need for more convenient methods from the viewpoint of green chemistry. We considered the possibility that the volatility and toxicity of OsO_4 could be masked by ionic liquids. Therefore, efficient recovery and reuse of OsO_4 might be possible by using ionic liquids. We describe here a novel olefin dihydroxylation by recoverable and reusable OsO_4 in an ionic liquid, $[emim]BF_4$.[8]

We examined the effects of various reaction conditions (solvents, quantities of OsO_4, and cooxidants) on osmium catalyzed dihydroxylation in the ionic liquid (Table 1). Reactions of 1,1-diphenylethylene (**1**) with 1.1–1.2 equiv. of cooxidants were carried out in several solvents at room temperature. The reaction with 5 mol% OsO_4 in $[emim]BF_4$ in the presence of 1.2 equiv. of *N*-methylmorpholine *N*-oxide monohydrate ($NMO{\cdot}H_2O$) proceeded smoothly to give the diol **2** in good yield (run 1).[9] Whereas the chemical yield was dramatically decreased when 1 mol% OsO_4 was used in $[emim]BF_4$, the addition of 10% aqueous Et_4NOH solution to the reaction mixture improved the yield to 44% (run 2 vs. run 3). It was thought that alkaline solution would favor rapid hydrolytic removal of the diol from the osmate.[10] Next, we examined the effect of using cooxidants other than $NMO{\cdot}H_2O$ (runs 4–6). We found that OsO_4-catalyzed reactions with other cooxidants such as 30% H_2O_2, sodium percarbonate, and *t*-BuOOH gave poor results. Anhydrous *N*-methylmorpholine *N*-oxide (NMO) retarded the reaction to afford **2** in 6% yield (run 7). This result is reasonable considering that the OsO_4-catalyzed reaction in ionic liquid required more than 1 equiv. of water to generate the diol from the coordination sphere of the osmium. In addition, it is noteworthy that the same reaction in

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Keywords: OsO_4; dihydroxylation; olefin; ionic liquid; $[emin]BF_4$.

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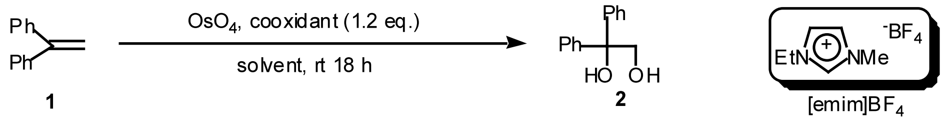
Table 1. Effects of solvents and cooxidants on OsO_4-catalyzed dihydroxylation of 1,1-diphenylethylene



Run	Solvent[a]	OsO_4 mol%	Cooxidant	Yield of **2**[b] %	Recovery of **1**[b] %
1	[emim]BF_4	5	$\mathrm{NMO\cdot H_2O}$	100	0
2	[emim]BF_4	1	$\mathrm{NMO\cdot H_2O}$	29	71
3	A	1	$\mathrm{NMO\cdot H_2O}$	44	56
4	[emim]BF_4	5	30%H_2O_2	2	96
5	[emim]BF_4	5	$\mathrm{Na_2CO_3\cdot 1.5\ H_2O_2}$	18	82
6	[emim]BF_4	5	*t*-BuOOH	31	18
7	[emim]BF_4	5	NMO	6	94
8	[emim]PF_6	5	$\mathrm{NMO\cdot H_2O}$	0	Complex mixture[c]

[a] [emim]BF_4 = 1-ethyl-3-methylimidazolium tetrafluoroborate; A = [emim]BF_4+Et_4NOH (0.1 equiv., 10% aqueous solution); [emim]PF_6 = 1-ethyl-3-methylimidazolium hexafluoroborate.

[b] Yields were determined by ^1H NMR.

[c] This reaction was carried out at 70°C because the melting point of [emim]PF_6 is 61°C.

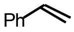
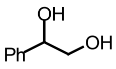
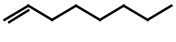
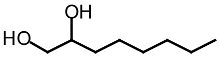
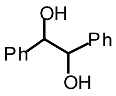
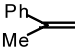
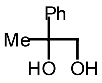
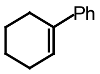
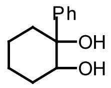
Table 2. Recovery and reuse of OsO_4 (5 mol%) in [emim]BF_4 using 1,1-diphenylethylene

Run	1	2	3	4	5
Yield (%)	95	93	96	95	93

[emin]PF_6 afforded no desired product (run 8). As described above, the reaction conditions in run 1 is the choice for good yield.

Next, we examined the possibility of recovery and reuse of OsO_4 in [emim]BF_4. After the first reaction had been completed, ethyl acetate was added to the reaction mixture in order to extract the diol. An orange–brown ionic liquid containing the catalyst was recovered, and this could be reused for further catalytic oxidation reaction. This procedure was repeated five times, and the results obtained are shown in Table 2 (runs 1–5).

Table 3. Dihydroxylation of olefins with OsO_4 in [emim]BF_4

Run	Olefin	Diol	Yield (%)
1			92
2			96
3			96
4			93
5			91

This new method using immobilized OsO_4 in an ionic liquid was applied to several substrates, including mono-, di-, and trisubstituted aliphatic olefins, as well as to aromatic olefins. The results are summarized in Table 3. In all cases, the desired diols were obtained in high yields (runs 1–5).

In summary, we have demonstrated the usefulness of recoverable and reusable immobilized OsO_4 in [emim]BF_4 for dihydroxylation of several olefins. This approach is simple and practical. It should be noted that the volatility and toxicity of OsO_4 are greatly suppressed when the ionic liquid [emim]BF_4 is used.[11] Examination of the applicability of our method to the asymmetric dihydroxylation of olefins is now in progress.

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8. This report was presented at the 122nd annual meeting of the Pharmaceutical Society of Japan (March 28, **2002**, 28[P]I-026, highlight). While we were preparing this report, the combination of OsO_4 and DMAP in [bmim]PF_6/water/*t*-BuOH for dihydroxylation of olefins was reported. Q. Yao. *Org. Lett.* **2002**, *4*, 2197–2199.
9. Typical reaction procedure is as follows. OsO_4 (0.1 mmol), [emim]BF_4 (2 mL), NMO·H_2O (2.2–2.4 mmol), and olefin (2 mmol) were added to a flask. Though [emim]BF_4 is immiscible with NMO·H_2O and olefin,[12] a completely homogeneous reaction mixture was formed after stirring. Then the reaction mixture was stirred at rt for 18 h under air atmosphere. The ionic liquid layer was extracted with ethyl acetate (4×15 mL). The combined extracts were concentrated and purified by flash silica gel column chromatography. Immobilized OsO_4 in [emim]BF_4 was able to be recovered almost quantitatively and was able to be reused for the next dihydroxylation.
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11. There was no volatile OsO_4 on the bottom of the septum of the reaction vessel after 3 months.
12. Ethyl acetate solution of olefins was used instead of liquid olefins when olefins were powder or crystals in order to avoid overoxidation of diols. Ethyl acetate was then removed under reduced pressure. Then the residue was similarly stirred.