

# Osmium-catalyzed dihydroxylation of alkenes by H<sub>2</sub>O<sub>2</sub> in room temperature ionic liquid co-catalyzed by VO(acac)<sub>2</sub> or MeReO<sub>3</sub>

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## Abstract

Room temperature ionic liquid [bmim]PF<sub>6</sub> was used to immobilize a bimetallic catalytic system for H<sub>2</sub>O<sub>2</sub>-based dihydroxylation of alkenes. Osmium tetroxide was used as the substrate-selective catalyst with either VO(acac)<sub>2</sub> or MeReO<sub>3</sub> as co-catalyst. The latter serve as an electron transfer mediator (ETM) and activates H<sub>2</sub>O<sub>2</sub>. For an increased efficiency *N*-methylmorpholine is required as an additional ETM in most cases. A range of alkenes were dihydroxylated using this robust bimetallic system and it was demonstrated that for some of the alkenes the catalytic system can be recycled and used up to five times.

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## 1. Introduction

Osmium-catalyzed dihydroxylation of alkenes is a synthetically important reaction and many oxidation systems have been developed for this transformation [1,2]. From an environmental point of view it is of interest to use oxidants such as hydrogen peroxide or molecular oxygen, which give no waste products [2–5].

We have recently developed several methods for the osmium-catalyzed dihydroxylation of alkenes by hydrogen peroxide [5–8]. The principle of these oxidation systems is that the hydrogen peroxide reacts with a co-catalyst (electron transfer mediator) to give a reactive peroxy or hydroperoxide intermediate, which efficiently can reoxidize Os(VI) to Os(VIII), often with the aid of an additional electron transfer mediator (ETM). The latter ETM, if required, is a redox catalyst that lowers the barrier for electron transfer and *N*-methylmorpho-

line/*N*-methylmorpholine-*N*-oxide (NMM/NMO) has been used for this purpose.

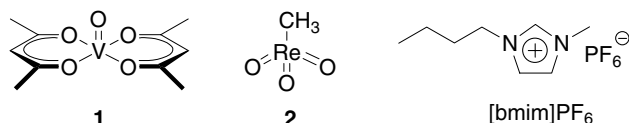
In the original version of the hydrogen peroxide-based dihydroxylation [5] an organocatalyst, a flavin, was used as the H<sub>2</sub>O<sub>2</sub>-activating catalyst. The flavin generates a flavin hydroperoxide, which rapidly oxidizes NMM to NMO in situ. The latter (NMO), in turn, rapidly oxidizes Os(VI) back to Os(VIII).

In a modified version of the H<sub>2</sub>O<sub>2</sub>-based dihydroxylation, VO(acac)<sub>2</sub> or MeReO<sub>3</sub> (MTO) was employed in place of the flavin for the activation of H<sub>2</sub>O<sub>2</sub> [6]. One problem encountered with MTO was that it underwent slow decomposition [9] under the reaction conditions employed. VO(acac)<sub>2</sub> worked better but also this co-catalyst was less efficient than the flavin employed in the original version.

Ionic liquids are attracting a growing interest as solvents for organometallic reactions [10,11]. The use of ionic liquids in osmium-catalyzed dihydroxylation was reported by four different groups in 2002 [12], and recently we [8] developed a H<sub>2</sub>O<sub>2</sub>-based version of the dihydroxylation in an ionic liquid. The latter procedure

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employed a flavin as the  $\text{H}_2\text{O}_2$ -activating catalyst. In the present paper, we report on a robust bimetallic catalytic system, employing co-catalysts  $\text{VO}(\text{acac})_2$  (**1**) and MTO (**2**) in an ionic liquid for the efficient dihydroxylation of alkenes by hydrogen peroxide.



## 2. Results and discussion

Dihydroxylation of alkenes by  $\text{H}_2\text{O}_2$  was carried out in the ionic liquid  $[\text{bmim}]\text{PF}_6$  with acetone as co-solvent employing  $\text{K}_2\text{OsO}_4$  as catalyst and either MTO or  $\text{VO}(\text{acac})_2$  as co-catalysts for  $\text{H}_2\text{O}_2$ -activation.

### 2.1. $\text{VO}(\text{acac})_2$ as co-catalyst

All reactions were carried out at room temperature with slow addition of hydrogen peroxide (8 h). Reaction of styrene with 30% aqueous hydrogen peroxide in  $[\text{bmim}]\text{PF}_6$ /acetone employing 2 mol% of  $\text{K}_2\text{OsO}_4$  and 2 mol% of  $\text{VO}(\text{acac})_2$  together with 23 mol% of *N*-methylmorpholine (NMM) afforded 81% diol after workup (Table 1, entry 1). Also,  $\beta$ - and  $\alpha$ -methylstyrene worked well and gave the corresponding diol in 82% and 91% yield, respectively (Table 1, entries 2 and 3). Several different alkenes were oxidized using these reaction conditions and the results are given in Table 1. Cyclohexene and acyclic aliphatic olefins gave good to high yields of the corresponding diols (Table 1, entries 6–10).

### 2.2. MTO as co-catalyst

The use of MTO as the  $\text{H}_2\text{O}_2$ -activating catalyst in osmium-catalyzed dihydroxylations is associated with the problem that MTO decomposes at alkaline pH by aq.  $\text{H}_2\text{O}_2$ . A solution to this problem was recently provided by allowing the reaction to occur under slightly acidic conditions [13]. We have now immobilized this system in ionic liquid  $[\text{bmim}]\text{PF}_6$  at room temperature. Reaction of styrene with hydrogen peroxide in  $[\text{bmim}]\text{PF}_6$ /acetone catalyzed by  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  (2 mol%) and MTO (2 mol%) in the presence of citric acid afforded the corresponding diol in excellent yield (Table 2, Method A, entry 1). Although the less basic protocol utilizing citric acid worked well for some of the olefins we encountered problems with cleavage of the double bond in the case of aliphatic olefins as well

as with some of the aromatic ones (Table 2, Method A). In particular, the more substituted aliphatic olefins were problematic. Thus, 1-octene was the only aliphatic olefin that gave a clean reaction and a high yield using only 5 mol% of citric acid (Table 2, entry 8).

Since the method based on citric acid gave considerable amounts of double bond cleavage for the aliphatic olefins, and it is well known that this cleavage is faster at lower pH, we replaced citric acid with tetraethyl ammonium acetate (TEAA) as in the  $\text{VO}(\text{acac})_2$ -co-catalyzed protocol. This proved to be successful and we obtained high yields for all the aliphatic olefins (Table 2, Method B, entries 7–10). Also the aromatic olefins worked quite well with this method to give satisfactory to good yields,

Table 1  
Osmium-catalyzed dihydroxylation of alkenes in ionic liquid using  $\text{VO}(\text{acac})_2$  as co-catalyst<sup>a</sup>

Entry	Olefin	Product	Yield <sup>b</sup>
1			81%
2			82%
3			91%
4			81%
5			73%
6			91%
7			80%
8			81%
9			86%
10			87%

<sup>a</sup> Experimental conditions: 7.2 mg of  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  (2 mol%), 5.3 mg of  $\text{VO}(\text{acac})_2$  (2 mol%), 25  $\mu\text{L}$  of *N*-methylmorpholine (NMM) (23 mol%), and  $\text{Et}_4\text{N}^+\text{OAc}^-$  (TEAA) (2 equiv.) were stirred in 0.5 mL of  $[\text{bmim}]\text{PF}_6$ , 3.8 mL of acetone and 1.2 mL of  $\text{H}_2\text{O}$  were added as co-solvents together with the olefin (1 mmol). 30%  $\text{H}_2\text{O}_2$  (1.5 mmol) was added over 8 h followed by 8 h of reaction.

<sup>b</sup> Isolated yields.

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