

# Oxidative cleavage of *vic*-diols catalyzed by manganese (III) complexes in ionic liquids

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Received 17 October 2007; received in revised form 13 November 2007; accepted 14 November 2007

Available online 4 December 2007

## Abstract

The oxidative cleavage of vicinal diols allows the selective oxidation of diols in order to obtain aldehydes or ketones. In this work we present a novel catalytic system based on Mn<sup>III</sup>(salen) complexes dissolved in ionic liquids that allows high efficiency with low environmental impact in the oxidative cleavage of ethyleneglycol, pinacol, benzopinacol and hydrobenzoin. The use of ionic liquids in this reaction shows a positive effect of the solvent in the efficiency of the Mn<sup>III</sup> catalysts (increase of the yield in ionic liquids: 10–60%).

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**Keywords:** Oxidative cleavage; Ionic liquids; Salen; Mn(III)-catalyst; *Vic*-diol

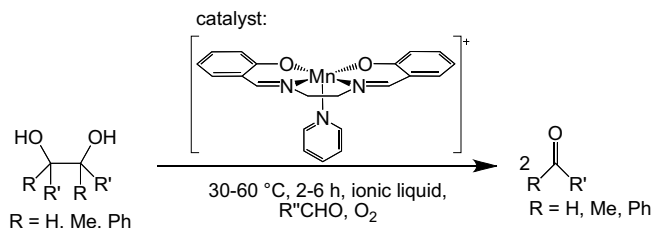
## 1. Introduction

The obtaining of aldehydes through the oxidative cleavage of vicinal diols is an important field in synthetic organic chemistry [1]. This type of reaction takes place in several important biochemical processes, such as the hydroxylated carbohydrates metabolism [2]. Nevertheless, although a wide range of systems from stoichiometric [1,3–7] to catalytic [8–12] have been tried, these are far away from the complete achievement in terms of activity, selectivity, atomic economy and environmental impact. Therefore, one of the aims of the organic synthesis is the development of new catalytic systems that allow the selective formation of aldehydes with non-polluting and non-toxic catalysts, using oxygen as an oxidant [9,13]. Our approach is based on the use of well known Mn<sup>III</sup>(salen) complexes [14,15] in ionic liquids (organic salts with low melting-point (<100 °C)) [16,17] as a catalytic system for the oxidative C–C bond cleavage of *vic*-diols to aldehydes with O<sub>2</sub> as oxidant and a sacrificial aldehyde as a

co-reductant [18]. The highly polar ionic liquids (IL) can stabilize the cationic catalyst or the ionic intermediates, having as a consequence an increased activity of the catalyst [19–21]. Furthermore, the option to recycle the catalyst/IL system as a strategy to improve the deficiency of the homogeneous catalysts allows also an improved total turnover number (TON) [22].

The selected catalysts are achiral manganese<sup>III</sup>(salen) complexes ((*N,N'*-bis(salicylidene)-1,2-ethylenediamine)-manganese (III)), which have been intensely investigated owing to their excellent performance in asymmetric alkene epoxidation [15]. The properties relating to activity, oxygen affinity and ligand modifications of these Mn(salen) complexes are well known, but so far they have not been reported in the catalytic oxidative C–C bond cleavage of vicinal diols. On the other hand, due to the environmental and economic necessity to recover and reuse homogeneous catalysts, they have been tried in the recycling of the catalyst/ionic liquid system for the Katsuki–Jacobsen epoxidation, showing that this type of catalyst can be reused without considerable loss of the activity [20,23]. The Mn<sup>III</sup> catalysts in ionic liquids therefore promise an alternative method for production of aldehydes and ketones from vicinal diols (Scheme 1).

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Scheme 1. Oxidative cleavage of vicinal diols catalyzed by  $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ .

## 2. Results and discussion

Considering the results reported by Pedro et al., using a tetradentate *o*-phenylenedioxamate manganese<sup>III</sup> catalyst [12] in which the substrate that presents the smaller reactivity is benzopinacol, we decided to select the best reaction conditions using manganese<sup>III</sup>(salen) complexes in ionic liquids with the sterically hindered tetraphenyl-1,2-ethanediol as a substrate. The tested diols were 1,2-ethanediol (ethyleneglycol, R = R' = H), 2,3-dimethyl-2,3-butanediol (pinacol, R = R' = Me), 1,2-diphenyl-1,2-ethanediol (hydrobenzoin, R = Ph, R' = H) and 1,1,2,2-tetraphenyl-1,2-ethanediol (benzopinacol, R = R' = Ph), so we could establish differences of reactivity as regards electronic and steric effects. Table 1 shows the results of the catalytic experiments (reaction conditions: 2–3 h, 30–60 °C, with constant bubbling of oxygen, 5 mol% of catalyst (*in situ* or isolated) and benzaldehyde or salicylaldehyde as sacrificial aldehyde) [24].

The catalytic activity of the Mn complexes toward the oxidative cleavage of vicinal diols shows better results in

ionic liquids than in organic solvents. The best oxidation condition is the use of oxygen as an oxidant in the presence of excess aldehyde as a sacrificial reagent, the so-called Mukaiyama catalytic system [18,25].

Also in the *in situ* system (the catalyst is formed from 5% mol of  $\text{Mn}(\text{OAc})_2$  with 1 equiv. of *N,N'*-bis(salicylidene)-1,2-ethylenediamine (salen), 1 equiv. of pyridine dissolved in dichloromethane/ionic liquid) there is improved activity if the reaction is carried out in ionic liquids as a solvent (entries 1–3, increasing of the yield from 18.4% in dichloromethane to 60.1% in  $[\text{OPic}][\text{PF}_6]$ ). The use of the isolated catalyst  $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$  allows us to obtain better yields (77.8% in dichloromethane and 82.9% in  $[\text{OPic}][\text{PF}_6]$ , entries 4–5). This indicates perhaps that the catalysis has a long induction time, and the formation of the catalytic species is better and faster if the isolated catalyst is used. Moreover, the Mn-catalyst in the ionic *N*-octyl-3-picolinium hexafluorophosphate is one of the more efficient systems for the C–C bond oxidative cleavage of 1,1,2,2-tetraphenyl-1,2-ethanediol, allowing a quantitative yield (>99%) after 2 h at 60 °C (entry 7). This result is definitively better than that reported by Pedro and co-workers using the *o*-phenylenedioxamate Mn<sup>III</sup> catalyst (in acetonitrile, at 40 °C, after 6 h: 10% yield) [12]. Although the role of the sacrificial aldehyde has not been clearly established, the Mukaiyama group proposed that for aerobic epoxidation reactions in the presence of this type of complex the reaction proceeds simultaneously with the co-oxidation of the aldehyde by a radicalic mechanism that generates a peroxyacid which reacts with the metallic complex to form an oxo intermediate [18,25]. We therefore evaluated the effect of two sacrificial aldehydes in the oxidative cleavage reaction of benzopinacol: benzaldehyde and salicylaldehyde.

Table 1  
Oxidative C–C bond cleavage of *vic*-diols catalyzed by manganese<sup>III</sup>(salen) complexes

Entry	R and R' substrate	Conditions	Solvent	%Yield <sup>a</sup>	
				Ketone	Aldehyde
1	R = R' = Ph	<i>In situ</i> (5% mol $\text{Mn}(\text{OAc})_2$ , salen, pyridine), 30 °C, 3 h, 3 equiv. benzaldehyde	Dichloromethane	18.3	
2	R = R' = Ph	<i>In situ</i> (5% mol $\text{Mn}(\text{OAc})_2$ , salen, pyridine), 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{BMIM}][\text{PF}_6]$	48.6	
3	R = R' = Ph	<i>In situ</i> (5% mol $\text{Mn}(\text{OAc})_2$ , salen, pyridine), 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{OPic}][\text{PF}_6]$	60.1	
4	R = R' = Ph	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	Dichloromethane	77.8	
5	R = R' = Ph	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{OPic}][\text{PF}_6]$	82.9	
6	R = R' = Ph	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 60 °C, 2 h, 3 equiv. benzaldehyde	$[\text{OPic}][\text{PF}_6]$	>99 <sup>b</sup>	
7	R = R' = Ph	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. salicylaldehyde	Dichloromethane	40.7	
8	R = R' = Ph	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. salicylaldehyde	$[\text{OPic}][\text{PF}_6]$	56.2	
9	R = R' = Me	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	Dichloromethane	43.2	
10	R = R' = Me	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{BMIM}][\text{PF}_6]$	58.5	
11	R = R' = Me	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{OPic}][\text{PF}_6]$	77.9	
12	R = H, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	Dichloromethane		0
13	R = H, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{BMIM}][\text{PF}_6]$		9.3 <sup>c</sup>
14	R = H, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. benzaldehyde	$[\text{OPic}][\text{PF}_6]$		30.2 <sup>c</sup>
15	R = Ph, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. salicylaldehyde	Dichloromethane		17.1
16	R = Ph, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. salicylaldehyde	$[\text{BMIM}][\text{PF}_6]$		43.2
17	R = Ph, R' = H	5 mol% $[\text{Mn}(\text{salen})(\text{Py})](\text{OAc})$ , 30 °C, 3 h, 3 equiv. salicylaldehyde	$[\text{OPic}][\text{PF}_6]$		41.0

<sup>a</sup> Yields (average of 2 runs) are for the isolated product, after purification by distillation or flash chromatography.

<sup>b</sup> No traces of the diol were detected after 2 h.

<sup>c</sup> Product derived with 2,4-dinitrophenylhydrazine.  $[\text{OPic}][\text{PF}_6]$ : *N*-octyl-3-picolinium hexafluorophosphate;  $[\text{BMIM}][\text{PF}_6]$ : butylmethylimidazolium hexafluorophosphate.

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