

# Salen-Mn(III)-Complex-Catalyzed Oxidations of Secondary Alcohols

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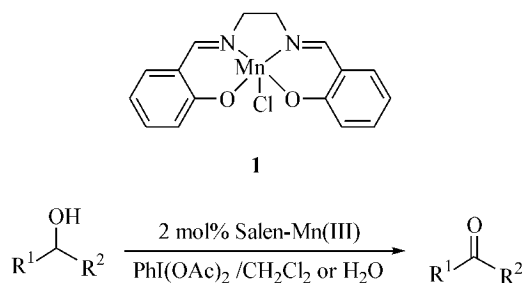
Secondary alcohols were catalytically oxidized with diacetoxyiodobenzene as oxidant in the presence of salen-Mn(III) complex to afford the corresponding ketones, in up to 99% yield, using CH<sub>2</sub>Cl<sub>2</sub> or water as reaction media.

**Keywords** salen-Mn(III) complex, oxidation, secondary alcohol, phase transfer catalyst

## Introduction

Carbonyl groups are the most important functional groups in organic synthesis, and their introduction by oxidation chemistry starting from alcohols is a process of major importance.<sup>1</sup> Early protocols for this transformation relied on the use of stoichiometric oxidants such as chromium(VI) reagents or MnO<sub>2</sub>.<sup>2</sup> With the goal of improving synthetic efficiency and avoiding potential environmental hazards, prominent success in this direction has been recently achieved by utilizing molecular oxygen with an assistance of potent transition metal compounds.<sup>3</sup> In the last few years, numerous terminal oxidant have successfully been employed in TEMPO-catalyzed oxidation of alcohols.<sup>4</sup> Recently, Iwasa *et al.*<sup>5</sup> reported that primary and secondary alcohols could be oxidized with diacetoxyiodobenzene [PhI(OAc)<sub>2</sub>] to afford the corresponding aldehydes and ketones in high yields when Ru(Pybox)(Pydic) complex was used as catalyst. Salen ligands are now recognized as efficient auxiliaries and many metallosalen complexes have been found to serve as excellent catalysts for a variety of asymmetric reactions such as epoxidation, aziridination, cyclopropanation, Diels-Alder reaction, and kinetic resolution of racemic epoxides, kinetic resolution of secondary alcohols, asymmetric ring opening of meso epoxides, enantioselective C—H amination and so on.<sup>6</sup> Adam found that Cr(salen) complexes were effective catalysts for the oxidation of secondary alcohols to ketones with diacetoxyiodobenzene [PhI(OAc)<sub>2</sub>] as oxidant.<sup>7</sup> Herein, we report a mild and effective procedure for the oxidation of secondary alcohols to ketones with good to excellent conversion, using catalytic amount of salen-Mn(III) complex with PhI(OAc)<sub>2</sub> as oxidant in CH<sub>2</sub>Cl<sub>2</sub> or water (Scheme 1).

Scheme 1



## Results and discussion

As indicated in Table 1, various types of secondary alcohols have been successfully oxidized. From the data in Table 1, it is clear that the reaction of aromatic alcohols to the corresponding carbonyl compounds is fast and efficient, except for *o*-methoxy-, *o*-chloro- $\alpha$ -methylbenzyl alcohol (Table 1, Entries 3, 4 and 6), whereas aliphatic alcohols reacted more slowly and the reactions were incomplete (Entries 10—13). The substitute of *ortho*-position is unfavorable for the oxidative reaction, which can be seen from Entries 4 and 6. In addition, in the case of *L*-menthol (Entries 8 and 9), the yield can not be enhanced greatly by increasing the catalyst quantity and reaction time.

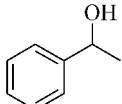
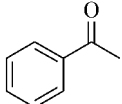
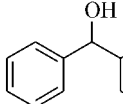
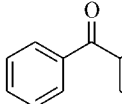
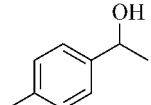
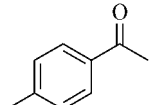
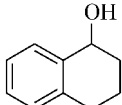
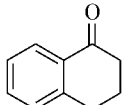
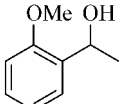
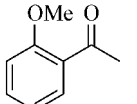
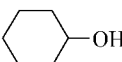
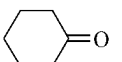
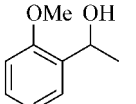
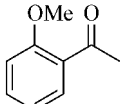
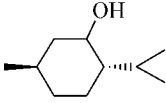
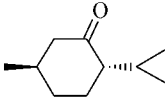
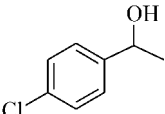
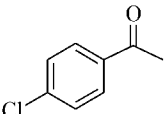
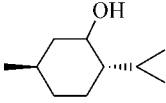
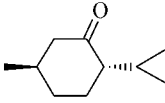
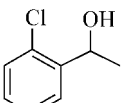
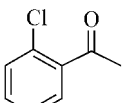
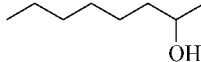
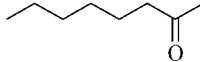
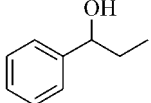
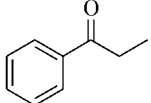
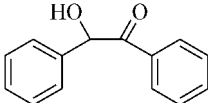
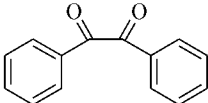
In the recent decades, chemists have begun investigating the possibility of using water as solvent for organic reactions, with some surprising and unforeseen results.<sup>8</sup> We initiated our investigation for an oxidation of alcohols in water using the same catalyst and oxidant, and the reaction results are shown in Table 2. Acetophenone was obtained in 65% yield (Table 2, Entry 1). Because the catalyst and substrate are insoluble in water, the phase transfer catalyst (PTC) tetraethylammonium bromide was added into the reaction system; acetophenone in 99% yield was attained for 2 h. From the data it can be seen that the rates of the reactions in water are faster than that in CH<sub>2</sub>Cl<sub>2</sub>. The reaction system was more environmentally

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**Table 1** Catalytic oxidation of secondary alcohols using salen-Mr(III) **1** as catalyst in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield <sup>b</sup> (%)	Entry	Substrate	Product	Time (h)	Yield <sup>b</sup> (%)
1			6	96	8			6	99
2			6	95	9			6	95
3			6	64	10			6	70
4			20	70	11			6	35
5			6	95	12 <sup>c</sup>			24	46
6			6	32	13			6	78
7			6	91	14			6	99

<sup>a</sup> Unless otherwise stated, the reaction conditions are: substrate (0.5 mmol), complex **1** (0.01 mmol), PhI(OAc)<sub>2</sub> (0.7 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL), room temperature. <sup>b</sup> GC yield based on the amount of substrate consumed. <sup>c</sup> Substrate (0.5 mmol), complex **1** (0.025 mmol), PhI(OAc)<sub>2</sub> (1.0 mmol).

benign because water was used as a reaction medium. Very recently, the chiral salen-Mr(III) complexes and PTC tetraethylammonium bromide catalytic system have been successfully applied in the oxidative kinetic resolution of secondary alcohols.<sup>9</sup>

In conclusion, we have developed a mild and highly efficient method for the oxidation of alcohols to the corresponding ketones with PhI(OAc)<sub>2</sub> as oxidant in organic solvent or in water. A more detailed study of this reaction is underway.

## Experimental

### Apparatus and reagents

The yields were determined by HP 6890 GC. The products were analyzed by Agilent 6890N/5973N GC-MS. PhI(OAc)<sub>2</sub> was purchased from Fluke Chemical Company and used as received.

### Preparation of complex **1**

The complex **1** was prepared following Jacobsen's procedure.<sup>10</sup>

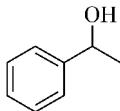
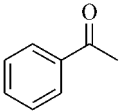
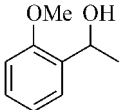
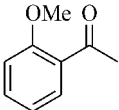
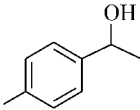
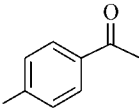
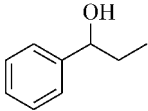
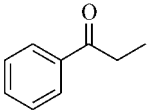
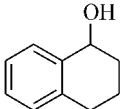
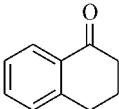
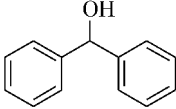
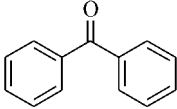
### General procedure for oxidations of secondary alcohols in CH<sub>2</sub>Cl<sub>2</sub>

A mixture of the substrate (0.5 mmol), catalyst (0.01 mmol), PhI(OAc)<sub>2</sub> (0.7 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was stirred in a 5-mL tube for 6–24 h at room temperature. When the reaction was over, the conversion was determined by GC.

### General procedure for oxidations of secondary alcohols in H<sub>2</sub>O

A mixture of the substrate (0.25 mmol), catalyst (0.005 mmol), tetraethylammonium bromide (0.02 mmol)

**Table 2** Catalytic oxidation of secondary alcohols using salen-Mr(III) **1** as catalyst in water<sup>a</sup>

Entry	Substrate	Product	Additive	Time (h)	Yield <sup>b</sup> (%)
1			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	4	65
2			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	1	91
3			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	2	99
4			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	3	67
5			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	2	98
6			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	2	97
7			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	2	89
8			$\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$	2	99

<sup>a</sup> Unless otherwise stated, the reaction conditions are: substrate (0.25 mmol), complex **1** (0.005 mmol),  $\text{PhI}(\text{OAc})_2$  (0.35 mmol),  $\text{H}_2\text{O}$  (1.0 ml), 0.02 mmol  $\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$ , room temperature. <sup>b</sup> GC yield based on the amount of substrate consumed.

and water (1 mL) was stirred in a 5-mL tube for a few minutes at room temperature, then oxidant  $\text{PhI}(\text{OAc})_2$  (0.35 mmol) was added to the reaction system, and stirred for a further 1–4 h. The products were extracted with diethyl ether when the reaction was over. The yields were determined by GC.

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