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Effective oxidation of benzylic and aliphatic alcohols with hydrogen peroxide catalyzed by a manganese(III) Schiff-base complex under solvent-free conditions

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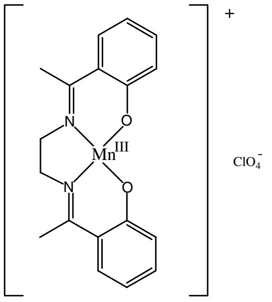
Abstract—A variety of alcohols were oxidized efficiently into the corresponding ketones and carboxylic acids in excellent yields with hydrogen peroxide using a manganese(III) Schiff-base complex as a catalyst under solvent-free and mild conditions. The oxidation procedure is very simple and the products are easily isolated in excellent yields.

The oxidation of alcohols is important in organic synthesis and the development of new oxidation processes continues to attract attention in spite of the availability of numerous oxidizing agents.[1,2] Recent demand for eco-friendly chemical processes has encouraged the development of clean reactions[3–15] and awaits further development of high yielding and economical methods for the oxidation of alcohols.[10]

Hydrogen peroxide has many advantages as an oxidant because water is the only by-product, which is easy to deal with after reactions. On the other hand, solvent-free reactions are of general interest because of their potential in combinational chemistry, simple processes, easy work-up, low cost and reduction in noxious waste materials. However, only a limited number of such useful oxidation procedures have been reported.[11–14] Although, a variety of different catalytic systems for the hydrogen peroxide-based oxidation of alcohols have been developed,[15–21] there is ongoing interest in the search for new efficient metal catalysts for this system.[9,22–26] Whilst the hydrogen peroxide oxidation of hydrocarbons catalyzed by Mn(IV) has been reported,[27,28] oxidation catalyzed with Mn(III) has received less attention.[29–35]

In continuation of our work on the selective oxidation of hydrocarbons,[36] we wish to report a very efficient and selective oxidation of benzylic and aliphatic alcohols into the corresponding ketones and carboxylic acids using hydrogen peroxide catalyzed by the Mn(III) Schiff-base complex **1**, under mild conditions. The complex was prepared by a procedure similar to that used by Karmaker et al.,[37] however, 1,2-diaminoethane was used instead of 1,3-diaminopropane.



1

To the best of our knowledge, there is no literature report on the oxidation of alcohols using a Mn(III) catalyst under our conditions. Oxidation of alcohols was performed at room temperature in the presence of a catalytic amount of the Mn(III) complex using H_2O_2 as the oxidant (Scheme 1) under solvent-free conditions.

Benzhydrol was selected as a model substrate for optimization of the process. A typical experimental

Keywords: Oxidation; Hydrogen peroxide; Catalyst; Selective oxidation; Mn(III) Complex; Alcohols.

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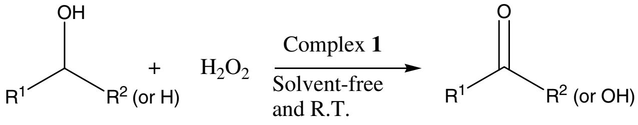


Scheme 1.

Table 1. Oxidation of benzhydrol to benzophenone[a]

Entry	Reaction time (h)	Conversion (%)
1	4.5	100
2[b]	12	<20
3[c]	12	NR[d]
4[e]	2.5	100
5[f]	12	100
6[g]	12	NR

[a] Unless otherwise indicated all reactions were carried out with 1 mmol of benzhydrol at room temperature with 0.1 mmol of Mn(III) catalyst **1** and 10 mmol of 30% aqueous H_2O_2.

[b] The reaction was carried out under an atmosphere of O_2 instead of H_2O_2.

[c] The reaction was carried out without Mn(III).

[d] NR: reaction did not occur.

[e] The temperature was increased to 50 °C.

[f] The concentration of Mn(III) was decreased to 0.05 mmol.

[g] The reaction was carried out with 0.1 mmol of Mn(III) acetate in place of complex **1**.

procedure was as follows: to the Mn(III) complex (0.1 mmol) was added the substrate alcohol (1 mmol), then hydrogen peroxide (10 mmol, 30%) was slowly added. The reaction mixture was stirred at room temperature until TLC indicated the reaction was complete. The residue was then washed with a minimal volume of solvent (methylene chloride, hexane or ether). Distillation of the solvent gave the product of acceptable purity. Oxidation took place to afford benzophenone in a 94% yield in the presence of **1** and 10 equiv of 30% H_2O_2 in 4.5 h (Table 1, entry 1). The large excess of hydrogen peroxide required was a result of its decomposition in the presence of the Mn(III) catalyst. The oxygen released in the decomposition played little role in the oxidation of the alcohols. The oxidation occurred only in poor yield by simply bubbling molecular oxygen through reaction mixture under similar reaction conditions (Table 1, entry 2). To evaluate the catalytic effect of complex **1**, the oxidation of benzhydrol was carried out under similar reaction conditions in the absence of catalyst and only the starting alcohol was recovered (Table 1, entry 3). Alternatively, the reaction was carried out at 50 °C under the same conditions in which, the oxidation was complete after 2.5 h (Table 1, entry 4). Further, when the oxidation of benzhydrol was carried out using less catalyst **1**,

Table 2. Oxidation of alcohols with hydrogen peroxide catalyzed by the Mn(III) complex under solvent-free and room temperature conditions[a]

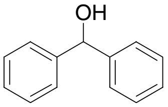
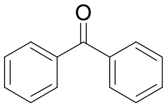
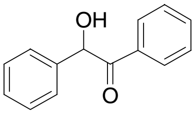
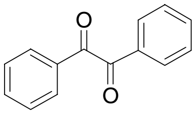
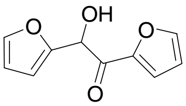
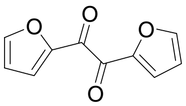
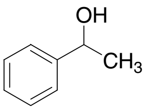
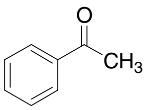
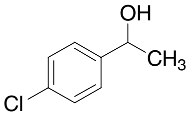
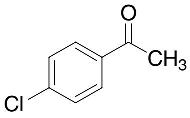
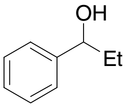
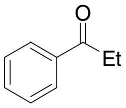
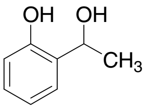
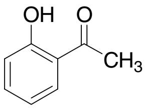
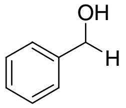
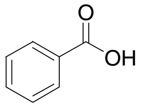
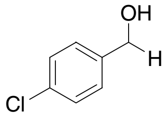
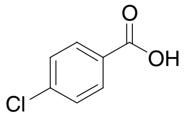
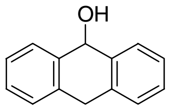
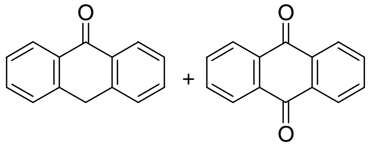
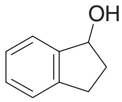
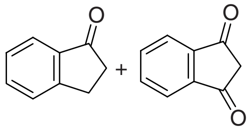
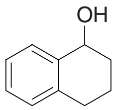
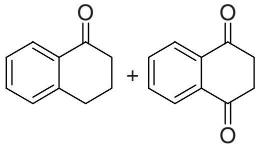
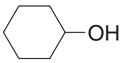
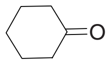
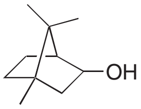
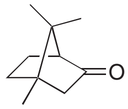
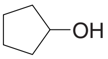
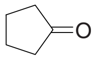
Entry	Substrate	Product[b]	Yield[c] (%)	Time (h)
1			94	4.5
2			93	4.5
3			97	4.0
4			95	5.5
5			95	4.5
6			97	5.0
7			93	4.5

Table 2 (*continued*)

Entry	Substrate	Product[b]	Yield[c] (%)	Time (h)
8			92	5.0
9			90	5.0
10			(80:16)	4.5
11			(83:14)	5.0
12			(80:12)	5.0
13[d]			98	14.0
14[d]			95	14.0
15			95	5.0

[a] 1 mmol of substrate at room temperature with 0.1 mmol of Mn(III) catalyst **1** and 10 mmol of 30% aqueous H_2O_2.

[b] The products were identified by comparison of physical and spectroscopic properties with authentic compounds.

[c] Isolated yields.

[d] An extra 10 mmol of H_2O_2 was added after 4.5 h. Without this extra addition a yield of 73% was obtained after 4.5 h.

the reaction was found to reach completion but over a much longer time (Table 1, entry 5). When other Mn(III) salts were used, such as Mn(III) acetate as a catalyst in place of complex **1**, no reaction took place and the starting material was recovered (Table 1, entry 6).

The oxidation of other benzylic alcohols was then examined using the optimized reaction conditions (Table 2). No oxidation was observed on the aromatic rings of the benzylic substrates. However, the alcohols in entries 10–12 behaved differently and benzylic oxidation also occurred to generate diketones as by-products (Table 2, entries 10–12).[36] The yields for the oxidation of aliphatic alcohols were about 95% (Table 2, entries 13–15). However, the reactions of cyclohexanol and borneol (Table 2, entries 13 and 14, respectively), required the addition of an extra 10 mmol % of H_2O_2 after 4.5 h.

As shown, the system was found to be selective and both aliphatic and benzylic alcohols were oxidized in excellent yields. The yields were confirmed after the products were isolated by short column chromatography using appropriate combinations of ethyl acetate/hexane. Although, almost quantitative conversion was observed by TLC, typically, 3–10% of product was lost during the work-up procedure.

Our results indicate that complex **1** is an effective catalyst for the hydrogen peroxide oxidation of alcohols under solvent-free conditions. An important advantage of this method aside from the solvent-free conditions is that it does not require a phase-transfer catalyst.

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