Oxidation of Alcohols with Hydrogen Peroxide Catalyzed by Molybdenum(VI)–Peroxo Complex under Solvent-free Conditions

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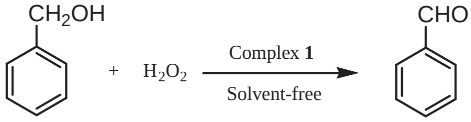
The oxidation of primary, secondary, allylic, and aromatic alcohols to the corresponding carbonyl compounds proceeds in high yield catalyzed by molybdenum(VI)–peroxo complex with H_2O_2 under solvent-free conditions. Secondary –OH group are selectively oxidized even in the presence of a primary –OH group. Products/catalyst separation can be easily carried out by simple extraction and the catalytic system can be reused without much loss of activity.

Over the years, the oxidation of alcohols to the corresponding carbonyl compound has been one of the most frequently used synthetic reactions in organic synthesis.[1] However, such transformations have been generally performed with environmentally hazardous inorganic oxidants, notably chromium(VI) reagents.[2] Therefore, from both the economic and environmental viewpoints,[3] there is a definite need for catalytic oxidation employing hydrogen peroxide as the stoichiometric oxidant. Because hydrogen peroxide is environmentally friendly, cheap, and readily available.[4] Recently, several different catalytic systems for the hydrogen peroxide oxidation of alcohols under solvent-free conditions have been developed.[5] For example, a variety of alcohols can be oxidized by a manganese(III) Schiff-base complex.[6] The DmpzHFC(cat.)–H_2O_2 system transforms primary, secondary, and allylic alcohols into their corresponding carbonyl compounds with good yields at room temperature.[7] Many molybdenum- and tungsten-based catalytic systems have been reported.[8] Noyori et al. have described tungstate-based biphasic systems, which are excellent in the oxidation of alcohol by H_2O_2 using a phase-transfer catalyst.[9]

In continuation of our work on the Mo^{VI} complexes,[10] we now report that the new Mo^{VI} oxo–diperoxo complex $[MoO(O_2)_2(TEDA)_2]$ (TEDA = 1,4-diazabicyclo[2.2.2]octane) (**1**), obtained through a simple approach of MoO_3 with H_2O_2 and TEDA, catalyzes the oxidation of a variety of alcohols to the corresponding carbonyl groups in high yields by H_2O_2. Although it is documented that under organic solvent conditions a variety of olefins,[11] sulfides,[12] alcohols,[13] and alkylbenzenes[14] can be oxidized by Mo^{VI} oxo–diperoxo complex and H_2O_2, to the best of our knowledge, there is no report regarding the oxidations of alcohols with H_2O_2 under solvent-free conditions.

Benzyl alcohol was first examined as a standard substrate with H_2O_2 in various solvents in the presence of a catalytic amount of **1**, indicating that the system without any solvent was the most effective one. The reaction was allowed to reflux at ca. 80 °C in the presence of 1 mol % of **1** for 6 h, which gave a 96% yield, 98% selectivity to benzaldehyde (Table 1, Entry 1). Using the non-polar solvents, such as toluene and dichloromethane (organic/aqueous biphasic system), gave benzaldehyde in the yields of 34 and 22%, respectively (Table 1, Entries 2 and 3), and water-miscible polar acetonitrile gave a 67% yield (Table 1, Entry 4). Controlled experiments without complex **1** showed no oxidation under the same reaction conditions (Table 1, Entry 5).

Table 1. Oxidation of benzyl alcohol with hydrogen peroxide in various solvents[a]



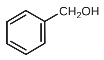
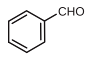
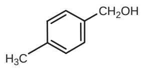
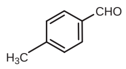
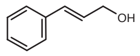
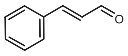
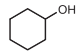
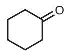
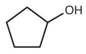
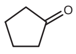
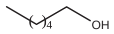
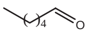
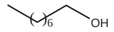
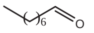
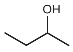
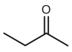
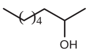
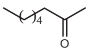
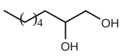
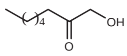
Entry	Solvent	Yield/%	Selectivity/%
1	—	96	98
2	Toluene	34	99
3	Dichloromethane	22	99
4	Acetonitrile	67	99
5[b]	— (no catalyst)	N. R.	

[a]Reaction conditions: Benzyl alcohol (1 mmol), **1** (0.01 mol, 1 mol %), 30% aqueous H_2O_2 (2 mmol), 6 h, 80 °C. Yields were determined by gas chromatography with an internal standard technique, and based on benzyl alcohol. [b]Reaction was carried out in the absence of catalyst.

To evaluate the scope of this reaction, the oxidation of a selection of primary, secondary, allylic, and aromatic alcohols was carried out with H_2O_2 in the presence of a catalytic amount of **1**. The results obtained are summarized in Table 2. Besides benzylic alcohols, the substrate having electron-releasing substituents, such as 4-methylbenzyl alcohol, was compatible with this system (Table 2, Entry 2). Benzyl alcohols could be oxidized to benzaldehydes in good yield with no over-oxidation. This behavior is simple to explain because of the reactivity of benzylic alcohols.[15] The oxidations of allylic and secondary cyclic were also examined upon treatment with complex **1**–H_2O_2; then they were converted to the corresponding aldehydes (Table 2, Entries 3–5).

The yields of oxidation of primary aliphatic alcohols were very low in the same condition. As shown, longer periods of reaction, greater quantities of catalyst and oxidant were needed for the oxidation of primary aliphatic alcohols (Table 2, Entries 6 and 7). But the catalytic oxidation could be successfully performed efficiently with secondary aliphatic alcohols (Table 2, Entries 8 and 9). It was notable that the secondary –OH group was chemoselectively oxidized to ketone even in the presence of a primary –OH group (Table 2, Entry 10). Trost and Masuyama[16] found the same selectivity in a molybdenum-catalyzed alcohol oxidation by hydrogen peroxide. It is assumed that selective oxidation of a secondary alcohol can be performed

Table 2. $[MoO(O_2)_2(TEDA)_2]$-catalyzed oxidation of selected alcohols using H_2O_2 as oxidant[a]

Entry	Substrate	Time/h	Product	Yield[b]/%	Selectivity/%
1		6		96	98
2		6		96	96
3		6		92[d]	93
4		8		90[d]	100
5		8		92	100
6[c]		16		86	86
7[c]		18		83[d]	83
8		10		91	91
9		10		88	88
10		10		89	89

[a]Reaction conditions: alcohol (1 mmol), **1** (0.01 mol, 1 mol %), 30% aqueous H_2O_2 (2 mmol), 80 °C, control experiments without complex **1** showed no oxidation under the same reaction conditions. [b]Determined by GC using an internal standard technique. [c]Complex **1** (0.05 mol, 5 mol %) and 30% H_2O_2 (5 mmol) were added. [d]Isolated yield.

when primary ones are hard to oxidize under the same condition.

The catalytic system left over can be reused for further catalytic oxidation. Oxidation products could easily be isolated by extraction since catalyst **1** was completely insoluble in these solvents. The only side product produced from hydrogen peroxide was water, and was removed under vacuum. The catalytic system containing the catalyst **1** could be reused without significant decrease of catalytic activity and selectivity. The recovered system was found to have comparable activity for up to three recycling experiments, yielding 94, 93, and 91%, in each cycle respectively (based on the oxidation of benzyl alcohol). We have found an important advantage to be that there is no need for a phase-transfer reagent, as in the solvent-free oxidations described previously.[9a,17]

For the sake of comparison, complexes $[MoO(O_2)_2(L)_2]$ (L = 1-azabicyclo[2.2.2]octane **2**, pyridine **3**) were also synthesized using the same method, except that 1-azabicyclo[2.2.2]-octane and pyridine were used respectively instead of TEDA. The yields obtained with complex **2** or **3** as the catalyst under identical conditions were very poor. For instance, benzyl alcohol (Entry 1) prepared to react with H_2O_2 and either **2** or **3** for 6 h gave an 18 or 23% yield respectively. Our experiment supports the view that the greater the solubility of a Mo^{VI}(cat)–H_2O_2 system, the better the yield for the oxidation of alcohols.

The proposed reason for the high effectiveness of **1** is that there is no solvent strongly coordinate to the molybdenum center when the catalyst dissolves in 30% hydrogen peroxide, with the result that structure of the catalyst is stable. On the other hand, because TEDA is a bidentate ligand, one site can coordinate to the metal center, while the other is exposed outside, resulting in an enhancement of the polarity of the complex molecule. Thus, the complex is relatively easy to dissolve in hydrogen peroxide.

In summary, this study represents the first Mo^{VI}–peroxo complex using aqueous hydrogen peroxide as oxidant; no halide and organic solvent was used in the whole process.

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