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A green and efficient oxidation of benzylic alcohols using H_2O_2 catalyzed by Montmorillonite-K10 supported $MnCl_2$

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Abstract

Primary and secondary benzylic alcohols were oxidized to the corresponding carbonyl compounds in good to high yields by environmentally friendly and green oxidant, H_2O_2 catalyzed by Montmorillonite-K10 supported manganese(II) chloride.

Keywords: Green oxidation system; Hydrogen peroxide; Montmorillonite-K10; Manganese(II) chloride

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Aldehydes and ketones represent an important class of products and intermediates in the fine chemicals and specialties [1]. The oxidation of alcohols to carbonyl compounds is an important transformation of organic synthesis, and several methods have been explored to accomplish such a conversion [2–10]. These methods involve the use of expensive reagents, long reaction times, strongly acidic condition and tedious work-up procedure leading to the generation of a large amount of toxic waste. Considering these facts, there is still a need to introduce new catalysts for this conversion.

Apart from molecular oxygen, recently, hydrogen peroxide has been a very attractive ‘green oxidant’ offering the advantages that it is cheap, environmentally benign, readily available and produces only water as a by-product [11]. Nevertheless, hydrogen peroxide alone has to be used carefully due to the possibility of an over-oxidation reaction [12].

Although a variety of different catalytic systems for the hydrogen peroxide oxidation of alcohols have been developed, there is a growing up interest in the search for new efficient metal catalysts for this concern. Clay and polymer supported reagents have been widely applied in organic synthesis mainly because of the ease of separation of products, readily availability commercial clays, simple workup, selectivity and mild reaction conditions. Montmorillonite clays have been extensively used as efficient supports for a variety of organic reagents [13].

During the courses of our systematic study on catalytic oxidation we have recently reported some salts supported on montmorillonite as a catalyst for the oxidation [14]. Here we report Montmorillonite-K10 supported manganese(II) chloride as a new catalyst for the oxidation of benzylic alcohols.

DMF was appropriate solvent for oxidation of primary and secondary benzylic alcohols for our purposes. Then we designed reactions without one of the reagents, catalyst and oxidant. The deoximation of benzyl alcohol carried out in presence of only $MnCl_2$ or H_2O_2 in separated route. We observed that in absent of catalyst or oxidant no reaction occurred. The results for oxidation of different primary and secondary benzylic alcohols are summarized in Table 1. It should be mentioned that all the reactions occurred with complete selectivity for aldehydes or ketones and no other

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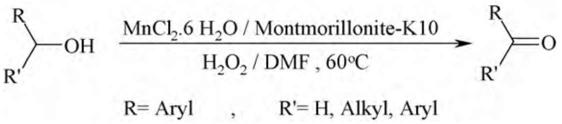
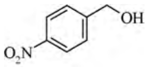
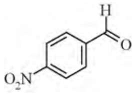
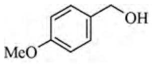
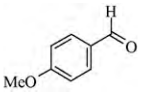
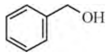
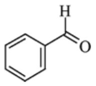
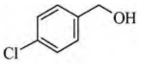
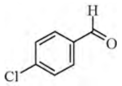
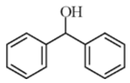
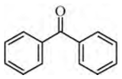
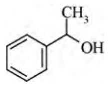
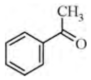
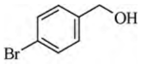
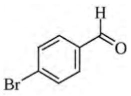
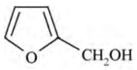
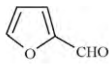
Table 1
Oxidation of various benzylic alcohols using H_2O_2 catalyzed by Montmorillonite-K10 supported $MnCl_2$.



Entry	Substrate[a]	Product[b]	Time (h)	Yield[c] (%)
1			4	97
2			2	95
3			5	99
4			4	95
5			3	88
6			4	78
7			4	98
8			6	95

[a] All substrates were synthesized by known literature procedures.

[b] All products were characterized by comparison of their mp as well as their IR and H NMR spectra with those of authentic samples.

[c] Yields refer to isolated products.

products were detected in the reaction mixture. The structures of products were confirmed by IR and ^{1}H NMR [15] and comparison with authentic samples.

To demonstrate the recyclability of the catalyst, it was reused at least three cycles for further oxidation without a significant decrease in yield (Table 2).

1. Experimental

The catalyst was prepared by the following procedure: Montmorillonite-K10 was added to a solution of manganese(II) chloride tetrahydrate in acetone (0.2 mmol g^{-1} montmorillonite).

The mixture was stirred at room temperature for 2 h. The solvent was then evaporated and the residue was dried at 115 °C for 5 h.

Table 2
Reuse of the catalyst for oxidation of benzyl alcohol.

Run	Yield (%)
1	99
2	99
3	97

To a solution of 1 mmol alcohol in 10 mL DMF, 1 g catalyst was added. The reaction mixture was stirred at 60 °C and about 2.5 mL H_2O_2 were added dropwise by the time indicated in Table 1. For example in deoximation of benzyl alcohol about 2.5 mL H_2O_2 were added gradually interim 5 h. The reaction progress was monitored by TLC (eluent: *n*-hexan:ethylacetate = 7:3).

The reaction mixture was cooled to room temperature and then filtrated to recover the catalyst. The filtrate was extracted with toluene/H_2O (15 mL/15 mL). The organic layer was dried over Na_2SO_4 and the solvent was then evaporated and the product purified by column chromatography over silica gel (eluent: *n*-hexane:ethylacetate = 7:3).

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