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Solvent free oxidation of alcohols with manganese dioxide

Ji-Dong Lou[a,*] and Zhi-Nan Xu[b]

[a]*Institute of Chemical and Biological Technology, New University of Lisbon, 2780 Oeiras, Portugal*
[b]*Department of Chemical Engineering and Bioengineering, Zhejiang University, Hangzhou, Zhejiang 310027, China*

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Abstract—The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones by manganese dioxide under solvent free conditions are described. This new oxidation procedure is very simple and affords good yields.

The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is a fundamental reaction that is encountered at all levels of organic synthesis. Manganese dioxide (MnO_2) is a useful selective oxidising reagent that is available for carrying out this transformation. For instance, the corresponding aldehydes or ketones can be obtained with MnO_2 by oxidation of allylic alcohols in petroleum ether, hexane, acetone or chloroform,[1–4] of propargylic alcohols in dichloromethane,[5–7] of benzylic or heterocyclic alcohols in chloroform, dioxane or acetone,[8–10] of saturated alcohols in petroleum ether or acetonitrile,[11] and by oxidative cleavage of 1,2-diols in dichloromethane.[12]

It is well known that the oxidation of organic compounds with MnO_2 has been performed in many solvents. The choice of the solvents is important. Thus primary or secondary alcohols (or water) are unsatisfactory since they can compete with the substrate being adsorbed on the MnO_2 surface and they have a strong deactivating effect.[13] A similar but less pronounced influence has also been observed with various polar solvents such as acetone, ethyl acetate, DMF, and DMSO. However, these polar solvents, including water,[14] acetic acid, and pyridine, should be used at higher temperatures. This deactivating influence due to the polarity of the solvent can be used to control the reactivity of active MnO_2 and sometimes to avoid side reactions or to improve the selectivity. In general, most of the reactions described in the literature are carried out in aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons, diethyl ether, THF, ethyl acetate, acetone, and acetonitrile.

As a part of our program related to developing new oxidation methods[15–22] we wish to report here a new, simple, and general procedure that can be used for the oxidative transformation of primary and secondary alcohols into the corresponding aldehydes and ketones using an inexpensive and environmentally friendly oxidant, MnO_2, under solvent free conditions. Solvent free reactions are of general interest because of their potential applications in combinatorial chemistry.

Active MnO_2 is prepared from potassium permanganate ($KMnO_4$) under basic conditions according to the literature.[23] The amount of active MnO_2 required to perform the oxidation of an alcohol substrate depends on the type of MnO_2 and on the substrate. In our cases, the ratio of MnO_2 to substrate is 10 to 1 by weight. The oxidation is very simple: the oxidant is added to the substrate in a flask in one portion and the mixture is stirred magnetically at room temperature until TLC analysis indicates a completed reaction. The residue is then washed with a minimum amount of solvent such as dichloromethane or diethyl ether. Distillation of the solvent gives a product that is of acceptable purity for most purposes. The results, which are shown in Table 1, show that the method is generally applicable to a range of alcohols, and gives the corresponding aldehydes and ketones in good yields. Meantime, we have observed that unactivated alcohols such as 1-hexanol or 1-octyl alcohol are not efficiently oxidised under these conditions.

In summary, solvent free oxidation using MnO_2 as an oxidant is a new and efficient method for the oxidation of primary and secondary alcohols.[24]

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Keywords: oxidation; alcohols; aldehydes; ketones; manganese dioxide; solvent free.

* Corresponding author. Fax: +351-21-44-03-609; e-mail: lou@itqb.unl.pt

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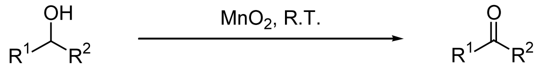
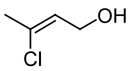
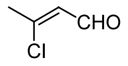
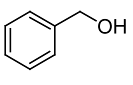
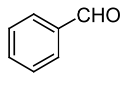
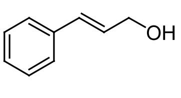
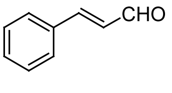
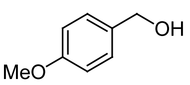
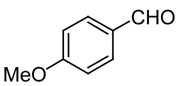
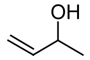
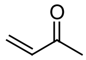
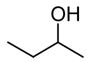
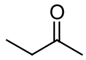
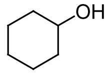
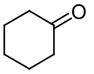
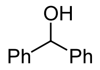
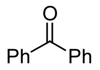
Table 1. Solvent free manganese dioxide oxidations



Substrate[a,b]	Reaction time (h)	Product[c]	Yield (%)
	24		81
	48		77
	24		87
	48		83
	24		70
	72		62
	72		67
	24		87

[a] For solid substrates the reaction temperature should be near or above their melting points.

[b] Caution! The mixture of manganese dioxide and an alcohol may potentially be dangerous. We have run each reaction at least 3 times on amounts ranging from 0.050 g to 0.150 g without encountering any problem. We nevertheless advise any user to take adequate precautions.

[c] All the aldehydes and ketones have been described previously in the literature and were identified by their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones.

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