Chemical Manganese Dioxide (CMD), an Efficient Activated Manganese Dioxide. Application to Oxidation of Benzylic and Allylic Alcohols

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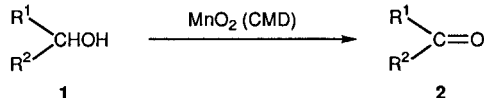
Abstract: Oxidation of benzylic and allylic alcohols with chemical manganese dioxide smoothly proceeded under mild reaction conditions to give the corresponding aldehydes and ketones, respectively, in high yields.

It is well-known that activated manganese dioxide (MnO_2) is a useful reagent both for selective oxidation of benzylic and allylic alcohols to aldehydes and ketones, respectively, and for dehydrogenation of heterocycles to heteroaromatics.[1] Although several methods for preparation of activated MnO_2 have been reported,[2] preparations are very tedious and sometimes the oxidation efficiency lacks reproducibility.

Commercially available activated MnO_2 can also be used, but again its activity varies widely. We have already reported that chemical manganese dioxide (CMD),[3] produced for dry battery manufacture, can be efficiently used for oxidation of some allylic alcohols[4] and for dehydrogenation of heterocycles such as thiazolines,[5] 2,3-dihydrofurans,[6] 3-pyrrolines,[7] and 2-pyrrolines.[8] Further investigations along this line have revealed that CMD is widely applicable to the selective oxidation of benzylic and allylic alcohols **1** to aldehydes and ketones **2**, respectively, as shown in Scheme 1.

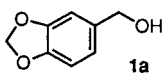
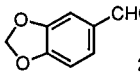
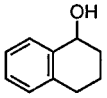
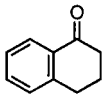
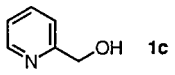
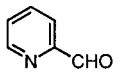
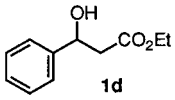
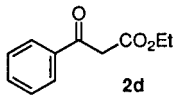
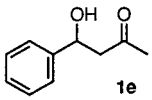
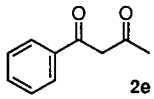
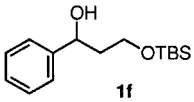
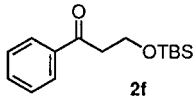
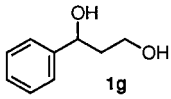
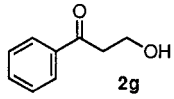
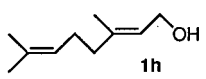
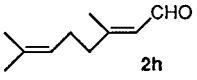
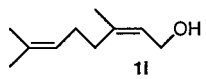
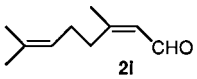
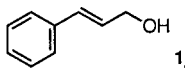
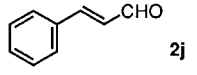
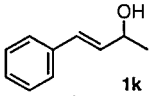
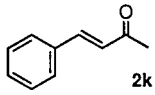
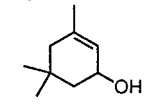
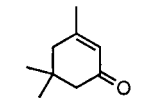


Scheme 1

A typical experimental procedure is as follows: A mixture of piperonyl alcohol **1a** (152 mg, 1 mmol) and CMD (869 mg, 10 mmol) in dichloromethane (10 ml) was stirred at room temperature for 24 h. The mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (Fuji Davison, BW-820 MH, 15 g, hexane : AcOEt = 10:1 to 5:1) to give piperonal **2a** (143 mg, 95 %).

The results are summarized in Table. Various benzylic and allylic alcohols **1** including functionalized ones smoothly underwent the oxidation with CMD to give the corresponding aldehydes and ketones **2** in high yields. No isomerization of double bond was observed in the oxidation of the cis- and trans-α,β-unsaturated alcohols **1h**~**k**. As compared with the reported procedure using activated MnO_2,[2,9-11] the efficiency of the method described here is either superior or comparable. In the oxidation of 1,2,3,4-tetrahydro-1-naphthol, CMD proved to be much superior to usual MnO_2 commercially available from Aldrich, Fluka, Merck, Nakarai, and Wako companies. Ten equivalents of CMD was usually required for completion of the reaction smoothly. Dichloromethane seemed to be the solvent of choice though benzene could be used.

Table. Oxidation of Benzylic and Allylic Alcohols with CMD

Starting Alcohol	Product	Yield [a,b] (%)
 **1a**	 **2a**	95
 **1b**	 **2b**	82 (92) [c]
 **1c**	 **2c**	52 [d] (89) [c] [68] [e]
 **1d**	 **2d**	80 [f]
 **1e**	 **2e**	50 [f]
 **1f**	 **2f**	87 [g]
 **1g**	 **2g**	57 [f,h]
 **1h**	 **2h**	81 [61~97] [i-k]
 **1i**	 **2i**	84
 **1j**	 **2j**	88 [70~77] [i,j]
 **1k**	 **2k**	85
 **1l**	 **2l**	71 [d]

a) Unless otherwise stated, the reaction was carried out as a typical procedure. b) Isolated yields. c) Determined by GLC. d) The reaction time was 5 h. e) Ref. 9. f) Twenty five equivalents of CMD was used. g) Thirty equivalents of CMD was used. h) The reaction time was 30 h. i) Ref. 2. j) Ref. 10. k) Ref. 11.

Incidentally, we found that the oxazolines **3a** and **3b**, bearing the aryl or vinilogous function at the C_2 position on the oxazoline ring, were smoothly dehydrogenated with CMD to give the oxazoles **4a** and **4b**, in good yields, as shown in Scheme 2. 1,2,3,4-Tetrahydroisoquinoline **5** also afforded 3,4-dihydroisoquinoline **6** with a small amount of isoquinoline **7** as a by-product.

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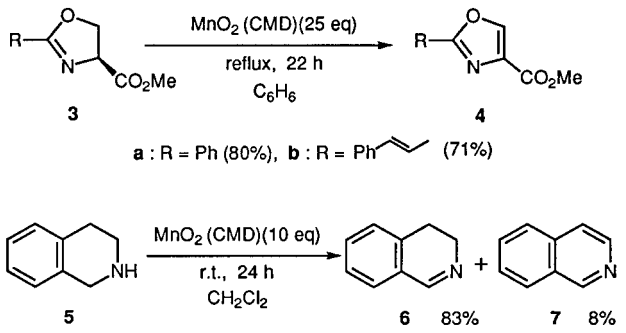

Scheme 2

The method described here is efficient and simple to conduct. Thus commercially available chemical manganese dioxide[3] in place of usual activated MnO_2 will be widely used for selective oxidation of benzylic and allylic alcohols to aldehydes and ketones.

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References and Notes

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