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# Oxidation by Chemical Manganese Dioxide. Part 3.[1] Oxidation of Benzylic and Allylic Alcohols, Hydroxyarenes and Aminoarenes†

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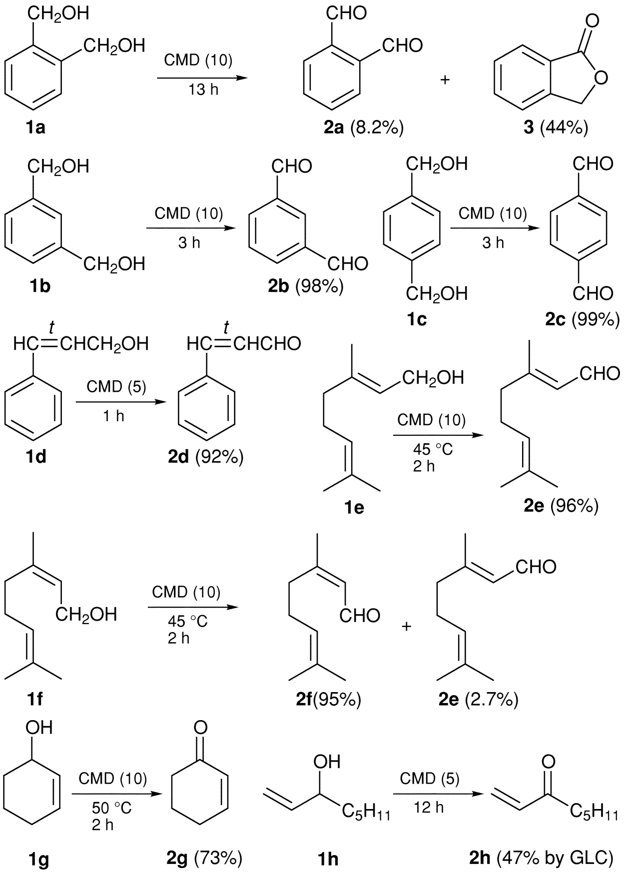
The combined use of chemical manganese dioxide (CMD) and molecular sieves in hexane (or in acetone) in general or CMD alone in particular cases enables the convenient and efficient oxidation of benzylic and allylic alcohols, phenols and amines under relatively mild conditions

We have recently reported in this journal on the use of chemical manganese dioxide (CMD)[2,3] for the oxidation of a series of benzylic monoalcohols[1a] and thiols,[1b] and the oxidative carbon–carbon bond cleavage of 1,2-diols,[1a] in which molecular sieves (MS) served as the efficient adsorbent of concomitantly formed water, allowing the easy work-up of products to be performed. The CMD–MS system leads to a selective and high-yielding oxidation, and thus can favorably be compared to conventional active manganese dioxide (AMD)-based oxidations.[4] Further studies have been performed in order to extend the scope of the CMD-based reaction, since the development of a new, convenient reagent system is invariably a fascinating challenge.

Reactions were in general carried out simply by efficiently stirring a heterogeneous mixture of a substrate, CMD and MS in gently refluxing hexane under an inert atmosphere. Oxidations of benzenedimethanols and allylic alcohols are illustrated in Scheme 1. Oxidation of benzene-1,2-dimethanol **1a** was slow and gave a mixture of phthalaldehyde **2a** and phthalide **3** in low and moderate yield respectively, even after prolonged reaction. In contrast, oxidation of 1,3- **1b** and 1,4-derivatives **1c** proceeded smoothly and produced isophthalaldehyde **2b** and terephthalaldehyde **2c**, respectively, in essentially quantitative yields. The poor reactivity of **1a** towards CMD could therefore be explained in terms of steric hindrance of the *o*-substituents as observed in the oxidation of substituted benzylic alcohols with CMD[1a] and also with AMD.[5] *trans*-Cinnamyl alcohol **1d** was readily converted to cinnamaldehyde **2d** without loss of the double bond stereochemistry. The CMD–MS system failed to bring about the selective oxidation of a polyene primary alcohol, nerol **1f**, to the *cis*-aldehyde **2f**, being accompanied by the formation of an appreciable amount of the *trans*-isomer **2e** ( > 10%). Attempted oxidation using CMD alone, however, was found to be effective for the selective oxidation of **1f** and also of geraniol **1e**. The absence of **1e** from the reaction mixture of **1f** coupled with the fact that **2f** is stable under the oxidation conditions might imply that the isomerization occurs during the intermediate stage of the oxidation under the influence of MS. Typical alicyclic **1g** and aliphatic allylic alcohols **1h** gave unsaturated ketones in moderate to good yield.



**Scheme 1** (No MS was added in the oxidation of **1e** and **1f**)

Di- and mono-hydroxyarenes were then treated with the CMD–MS system (Scheme 2). Oxidation of catechol **3a** in hexane gave a mixture of the *o*-quinone **4a** and an unknown product, but a repeat run in the acetone produced **4a** exclusively. 1,4-Benzoquinones **4c**–**e** can be obtained in excellent yields from hydroquinones **3c**–**e**. AMD oxidation of **3c** gave quinhydrone,[6] a binary 1:1 complex derived from **3c** and **4c**, in certain cases, but it was absent in the present reaction. On the other hand, resorcinol **3b** was inert under the oxidation conditions used for **3a** and **3c**, the substrate being recovered essentially unchanged. Phenols **3f** and **3g** underwent *p*,*p*- and *o*,*o*-couplings easily to give the diphenoquinone **4f** and the bisphenol **4g**, respectively. In addition, some aminoarenes **5a**–**d** can successfully be oxidised with the CMD–MS system (Scheme 3).

Although the CMD-based system requires elevated temperature to achieve the reaction at a reasonable rate, it can oxidise a number of functional groups in high yields. Indeed, yields of unsaturated aldehydes, **2d** (92%) and **2e** (96%), and the quinone **4c** (96%), for example, are much higher than those from typical AMD oxidations (Goldman's procedure[7] using azeotropically activated AMD in benzene,

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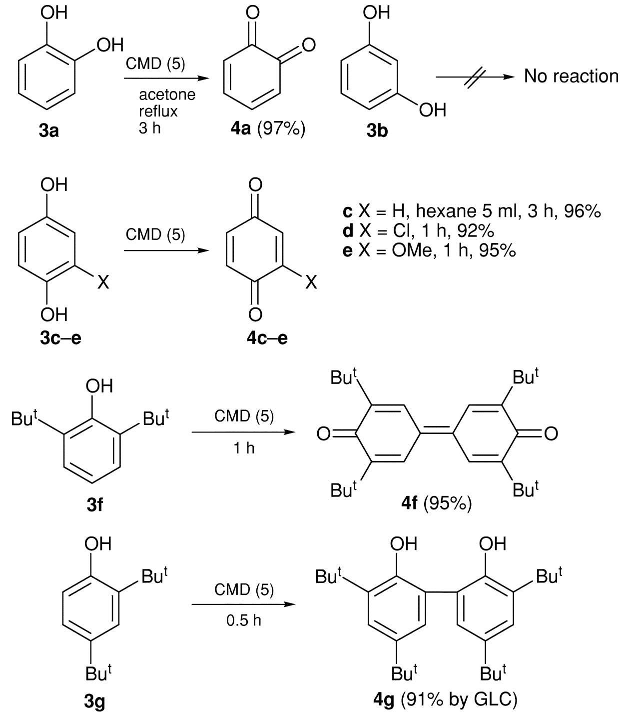


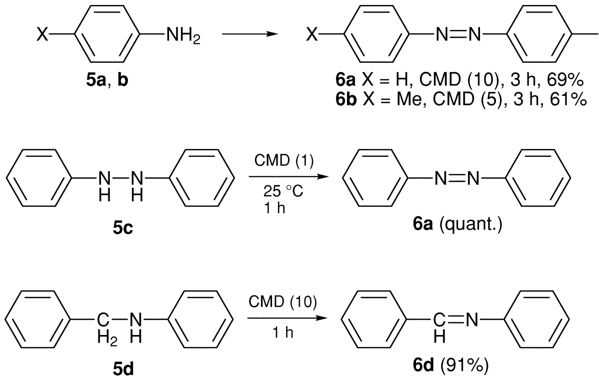
**Scheme 2**

at room temperature, 1–2 h; 70% as the 2,4-dinitrophenylhydrazone, 80% by GLC, and 65%, respectively). Consequently, it could reasonably be concluded that CMD is an inexpensive, attractive laboratory reagent that has extensive use for the oxidation of a variety of functional groups.[1]

## Experimental

Molecular sieves 4A powder (Aldrich) was oven-dried (350 °C, 6 h) prior to use. CMD (Wako) was used as received. Substrates to be oxidised were commercial chemicals, most of which were used as received from suppliers, but impure materials were purified by distillation or recrystallization prior to use. Hexane was dried ($CaCl_2$), distilled, and stored over molecular sieves. Mps were determined on a Yanagimoto MP-S3 melting point apparatus and are uncorrected. Mass spectra were determined on a JEOL SX-102A mass spectrometer coupled to a Hewlett Packard GC5890 Series II GC apparatus *via* a heated capillary column. GLC was performed on a Shimadzu GC-4BM or GC-4CM instrument equipped with a FID through a 2 m × 5 mm diameter glass column packed with 5% PEG-20 M on Chromosorb WAW-DMCS or 3% OV-17 on Uniport HP, respectively, and interfaced with a Shimadzu Chromatopac C-R6A integrator, with temperature programming.

*Oxidation Procedure*.—This was similar to that described previously.[1] Oxidations were carried out using the substrate (1 mmol), CMD (concentrations in mmol are given in parentheses) and predried MS (0.5 g) in gently refluxing hexane (10 ml) unless otherwise indicated in Schemes 1–3. Reactions achieved 100% conversion within the periods of time indicated, except for the cases of substrates **1a** and **1h** where unreacted substrates were detected by GLC (12 and 25%, respectively). Products were identified by comparison of their spectroscopic and/or physical data with those of commercial or independently prepared authentic samples.



**Scheme 3**

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