

SYNLETT
Spotlight 225

Synthetic Applications of Manganese Dioxide

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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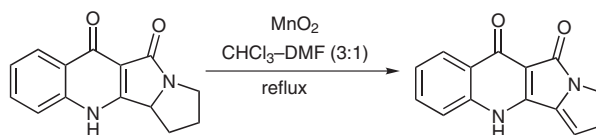
Introduction

The first report of activated MnO_2 as an organic oxidant was published in 1948, when it was found to give excellent yields of retinal from vitamin A.¹ Manganese dioxide as an oxidizing agent has been used extensively for the oxidation of a variety of functional groups, especially for the transformation of benzylic and allylic alcohols to their

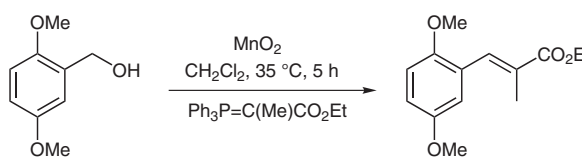
corresponding carbonyl compounds.² Manganese dioxide is one of the most attractive inorganic materials not only because of its physical and chemical properties and wide range of applications in catalysis, ion exchange, molecular adsorption, biosensor, and particularly energy storage,^{3,4} but also because of its low cost and environmentally benign nature.

Abstracts

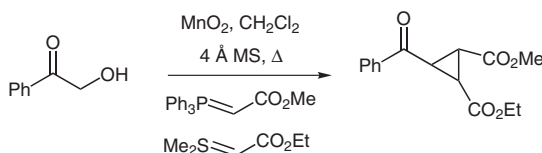
(A) Abe et al. showed the first total synthesis of quinolactacide. The synthetic route was concluded with reaction of the dehydrogenation with manganese dioxide in a mixture of chloroform and *N,N*-dimethylformamide.⁵



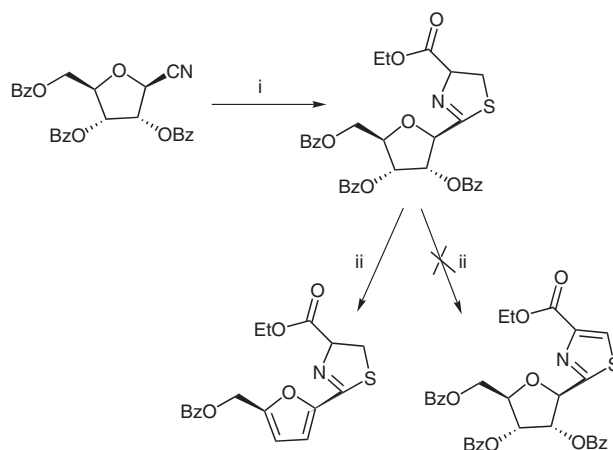
(B) Taylor et al. reported the first 'tandem oxidation process' (TOP) sequence for the synthesis of bromodienoate esters. Oxidations with MnO_2 followed by Wittig reactions have been extensively explored for the elaboration of alcohols to give conjugated alkenes, without the need to isolate the intermediate aldehydes.⁶



(C) Taylor and co-workers also described the manganese dioxide tandem oxidation–olefination–cyclopropanation sequence, in which the alcohol is treated with MnO_2 , phosphorane, and sulfurane, respectively. The oxidation–olefination reaction is followed by in situ cyclopropanation of the intermediate γ -ketocrotonate.⁷

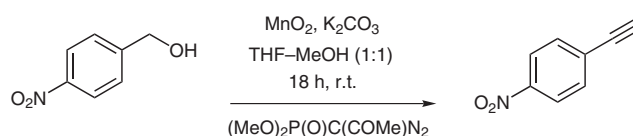


(D) Ramasamy et al. reported the MnO_2 oxidation of a thiazoline to a thiazole but also with elimination of the 2',3'-benzoate groups to form a furan ring. When they tried the dehydrogenation of the thiazoline intermediate with *N*-bromosuccinimide, followed by the addition of DBU, they also obtained the reaction product of the elimination of the 2',3'-benzoate groups. The formation of the elimination product of the thiazoline intermediate may have occurred through a radical intermediate. This is the first report where elimination of benzoate groups under radical conditions is shown.⁸

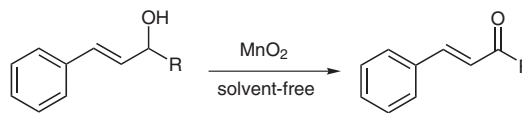


Reagents and conditions: (i) cysteine ethyl ester hydrochloride, Et_3N ; (ii) MnO_2 , benzene.

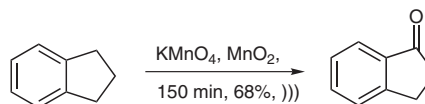
(E) The TOP sequence developed by Taylor was used coupled with the Bestmann–Ohira reagent. Using *p*-nitrobenzyl alcohol (1 equiv), MnO_2 (5 equiv), Bestmann–Ohira reagent (1.2 equiv), and K_2CO_3 (2 equiv) in THF–MeOH (1:1) at r.t. for 18 h, the terminal alkyne was obtained in 89% isolated yield.⁹



(F) Firouzabadi et al. showed that the use of MnO_2 in the absence of solvent has been applied successfully for the oxidation of benzylic alcohols to give the corresponding aldehydes or ketones in excellent yields. Aromatic allyl alcohols were oxidized by MnO_2 in excellent yields to the corresponding carbonyl compounds in the presence of 2 molar equivalents of the reagents.¹⁰



(G) Shaabani et al. reported that indans are converted into the corresponding α -ketones in good yields at room temperature in the absence of solvent and under microwave irradiation. The products obtained under these conditions are identical to those obtained from heterogeneous reactions where the oxidant is dispersed in dichloromethane.¹¹



References

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