SYNLETT
# Spotlight 225

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

# Synthetic Applications of Manganese Dioxide

Compiled by Eufrânio Nunes Silva da Júnior

Eufrânio Nunes da Silva Júnior was born in Brasília/DF, Brazil in 1982. He received his degree in Chemistry from Universidade Católica de Brasília (UCB), Taguatinga/DF, Brazil in 2004. Currently he is in the final stages of his M.Sc. studies under the supervision of Profs. Vitor Francisco Ferreira and Maria Cecilia B. V. de Souza in Organic Chemistry at Universidade Federal Fluminense. His research interests focus on the synthesis of naphthoquinones derivatized from lapachones and nor-lapachones and on the chemistry of heterocycles.

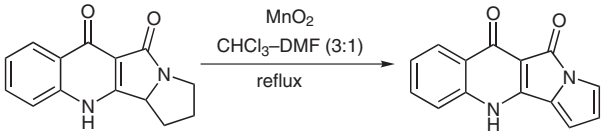
Instituto de Química, Universidade Federal Fluminense, UFF, 24020-150 Niterói, Rio de Janeiro, Brazil
E-mail: junior_uff@yahoo.com.br

## Introduction

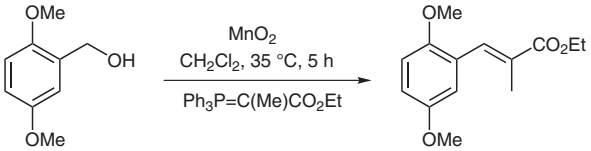
The first report of activated $MnO_2$ as an organic oxidant was published in 1948, when it was found to give excellent yields of retinal from vitamin A.[1] Manganese dioxide as an oxidizing agent has been used extensively for the oxidation of a variety of functional groups, especially for the transformation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

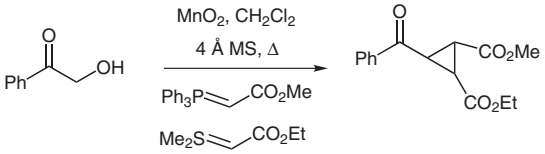
(A) Abe et al. showed the first total synthesis of quinolactacide. The synthetic route was concluded with reaction of the dehydrogenation with manganese dioxide in a mixture of chloroform and *N*,*N*-dimethylformamide.[5]




(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]

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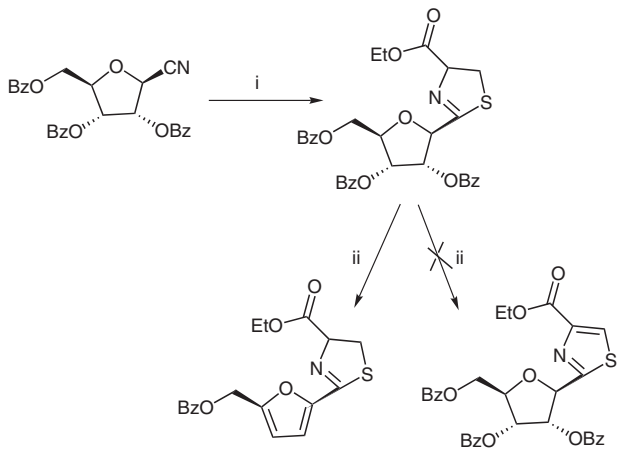
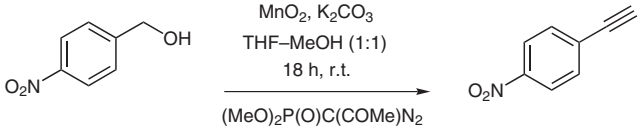
(D) Ramasamy et al. reported the $MnO_2$ oxidation of a thiazoline to a thiazole but also with elimination of the 2′,3′-benzoate groups to form a furan ring. When they tried the dehydrogenation of the thiazoline intermediate with *N*-bromosuccinimide, followed by the addition of DBU, they also obtained 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]

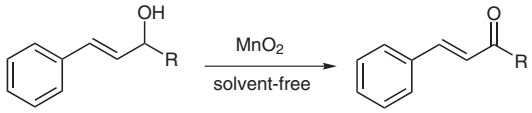



Reagents and conditions: (i) cysteine ethyl ester hydrochloride, $Et_3N$; (ii) $MnO_2$, benzene.

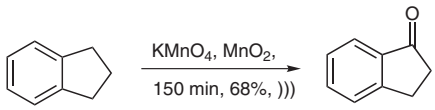
(E) The TOP sequence developed by Taylor was used coupled with the Bestmann–Ohira reagent. Using *p*-nitrobenzyl alcohol (1 equiv), $MnO_2$ (5 equiv), Bestmann–Ohira reagent (1.2 equiv), and $K_2CO_3$ (2 equiv) in THF–MeOH (1:1) at r.t. for 18 h, the terminal alkyne was obtained in 89% isolated yield.[9]




(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

(1) Ball, S.; Goodwin, T. W.; Morton, R. A. *Biochem. J.* **1948**, *42*, 516.
(2) (a) Fatiadi, A. J. *Synthesis* **1976**, 65. (b) Fatiadi, A. J. *Synthesis* **1976**, 133.
(3) Nalwa, H. S. *Handbook of Nanostructured Materials and Nanotechnology*; Academic Press: New York, **2000**.
(4) Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
(5) Abe, M.; Imai, T.; Ishii, N.; Usui, M. *Biosci., Biotechnol., Biochem.* **2006**, *70*, 303.
(6) Taylor, R. J. K.; Reid, M.; Foot, J.; Raw, S. A. *Acc. Chem. Res.* **2005**, *38*, 851.
(7) McAllister, G. D.; Oswald, M. F.; Paxton, R. J.; Raw, S. A.; Taylor, R. J. K. *Tetrahedron* **2006**, *62*, 6681.
(8) Ramasamy, K. S.; Bandaru, R.; Averett, D. *J. Org. Chem.* **2000**, *65*, 5849.
(9) Quesada, E.; Raw, S. A.; Reid, M.; Roman, E.; Taylor, R. J. K. *Tetrahedron* **2006**, *62*, 6673.
(10) Firouzabadi, H.; Karimi, B.; Abbassi, M. *J. Chem. Res., Synop.* **1999**, 236.
(11) Shaabani, A.; Mirzaei, P.; Naderi, S.; Lee, D. G. *Tetrahedron* **2004**, *60*, 11415.



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