

SYNLETT Spotlight 41

Manganese(III) acetate

Compiled by Grégory Bar



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

Grégory Bar was born in 1976 in Béthune (France). He obtained his engineer diploma in 1999 at the ENSSPICAM in Marseille. He is currently in his third year of D.Phil. at the University of York, working with Dr A. F. Parsons and Dr C. B. Thomas on the development of new manganese(III) acetate mediated reactions, for the synthesis of natural products.

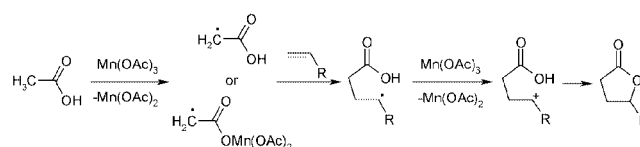
Department of Chemistry, University of York,
Heslington YO10 5DD, York, UK
E-mail: Gb120@york.ac.uk

Introduction

Metal-mediated oxidative radical cyclisations have become a very important method in synthetic chemistry over the last 40 years.¹ Of particular importance is the use of $\text{Mn}(\text{OAc})_3$ which acts as a one-electron oxidant. In 1968, it was shown to oxidise acetic acid leading to γ -lactones in the presence of alkenes.^{2,3} The mechanism of these reactions is not fully understood but is thought to proceed as shown in Scheme 1. Since then, a variety of alternative substrates to acetic acid, especially enolisable 1,3-dicarbonyls, have been successfully employed in related reactions, particularly cyclisations, to form 5- and 6-membered rings.⁴ The solvent of choice is acetic acid; oth-

er solvents (EtOH, CH_3CN , DMSO) tend to give lower yields.⁴

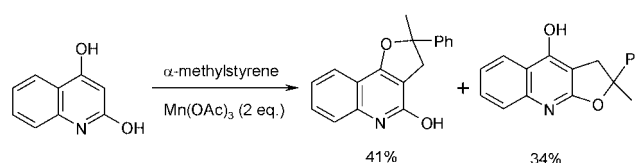
As $\text{Mn}(\text{OAc})_3$ is troublesome to prepare and highly deliquescent, the dihydrate form of the complex $[\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}]$ is generally used and this is commercially available.^{5,6}



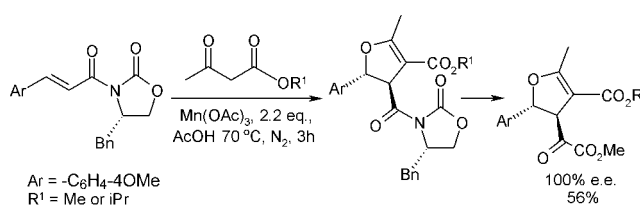
Scheme 1

Abstracts

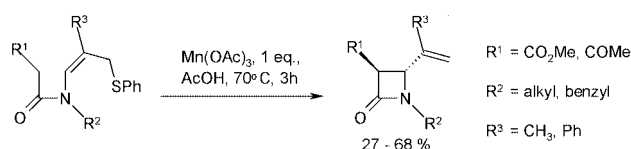
$\text{Mn}(\text{OAc})_3$ is generally used to form radicals at the α -position of carbonyls and particularly 1,3-dicarbonyls (e.g. 1,3-diketones, β -keto-esters and β -keto-amides), which can react with electron-rich alkenes. Acidic compounds such as quinolinediols, undergo fast enolisation leading to rapid oxidation forming angular and linear tricycles in good yields.⁷



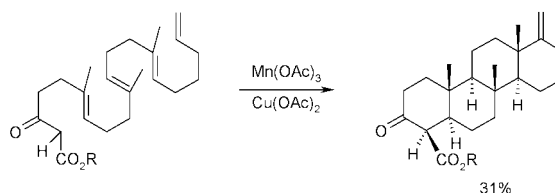
Stereoselective transformations are possible and the use of oxazolidinone chiral auxiliaries can lead to dihydrotetrahydrofurans with excellent ee.⁸



The formation of 4- as well 5- and 6-membered rings is possible as exemplified by the formation of *trans*- β -lactams in yields ranging from 27% to 68%⁹ using a radical cyclisation-fragmentation strategy.



Tetracyclisations can also be carried out; the copper(II) acetate facilitates the oxidation of the primary radical, leading to the steroid analogue as a single isomer (there is a possibility of 64).¹⁰



Although manganese(III) acetate is inexpensive its use on an industrial scale is problematic because 2 equivalents of the reagent is usually required to bring about the desired transformation and this generates considerable amounts of metal wastes. Chemical¹¹ and electrochemical¹² meth-

ods have been investigated to regenerate the manganese(III) in situ.

Related compounds including $\text{Mn}(\text{pic})_3$ in DMF [manganese(III)picolinate]¹³ and $\text{Mn}(\text{acac})_3$ [manganese(III) acetoacetate]¹⁴ are capable of initiating similar reactions.

References

- (1) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519.
- (2) Heiba, E. I.; Dessau, R. M.; Koehl, W. J. Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5905.
- (3) Bush, J. B. Jr.; Finkbeiner, H. J. *J. Am. Chem. Soc.* **1968**, *90*, 5903.
- (4) (a) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (b) Melikyan, G. G. *Aldrichimica Acta* **1998**, *31*, 50.
- (5) Midgley, G.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1537.
- (6) $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ are commercially available.
- (7) Bar, G.; Parsons, A. F.; Thomas, C. B. *Tetrahedron* **2001**, *57*, 4719.
- (8) Garzino, F.; Méou, A.; Brun, P. *Tetrahedron Lett.* **2000**, *41*, 9803.
- (9) Atteni, B.; Cerreti, A.; D'Annibale, A.; Resta, S.; Trogolo, C. *Tetrahedron* **1998**, *54*, 12029.
- (10) Zoretic, P. A.; Weng, X.; Caspar, M. L.; Davis, D. G. *Tetrahedron Lett.* **1991**, *32*, 4819.
- (11) Linker, U.; Kersten, B.; Linker, T. *Tetrahedron* **1995**, *51*, 9917.
- (12) Coleman, J. P.; Hallcher, R. C.; Mackins, D. E.; Rogers, T. E.; Wagenknecht, J. M. *Tetrahedron* **1991**, *47*, 809.
- (13) Iwasawa, N.; Funahashi, M.; Hayakawa, S.; Narasaka, K. *Chem. Lett.* **1993**, 545.
- (14) Nishino, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1922.