

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

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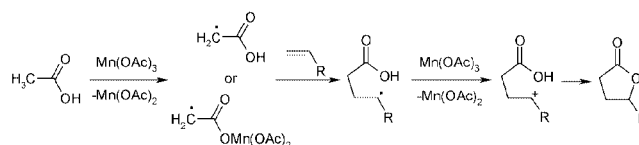
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Introduction

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; other

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

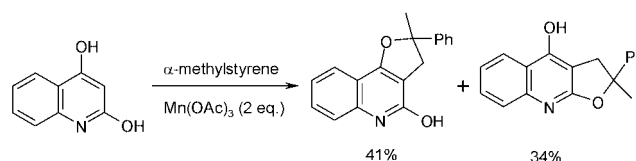
As $\text{Mn}(\text{OAc})_3$ is troublesome to prepare and highly deliquescent, the dihydrate form of the complex $[\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}]$ is generally used and this is commercially available.^{5,6}



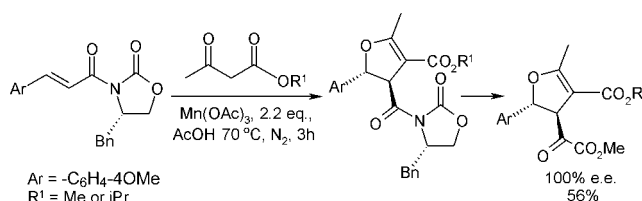
Scheme 1

Abstracts

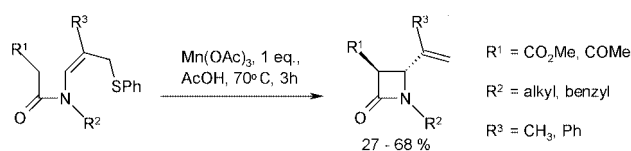
$\text{Mn}(\text{OAc})_3$ is generally used to form radicals at the α -position of carbonyls and particularly 1,3-dicarbonyls (e.g. 1,3-diketones, β -keto-esters and β -keto-amides), which can react with electron-rich alkenes. Acidic compounds such as quinolinediols, undergo fast enolisation leading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



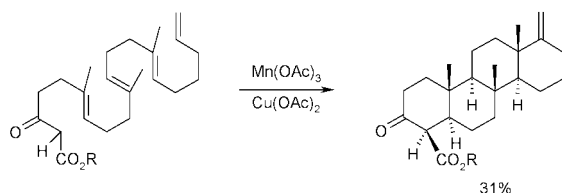
Stereoselective transformations are possible and the use of oxazolidinone chiral auxiliaries can lead to dihydrotetrahydrofurans with excellent ee.⁸



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.