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 Mn(OAc)\(_3\), which acts as a one-electron oxidant. In 1968, it was shown to oxidise acetic acid leading to \(/c103\)-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-dicarboxylics, 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\(_3\)CN, DMSO) tend to give lower yields.\(^4\)

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

![Scheme 1](image1.png)

Abstracts

Mn(OAc)\(_3\) is generally used to form radicals at the \(\alpha\)-position of carbonyls and particularly 1,3-dicarboxylics (e.g. 1,3-diketones, \(\beta\)-keto-esters and \(\beta\)-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-\(\beta\)-lactams in yields ranging from 27% to 68%\(^9\) using a radical cyclisation-fragmentation strategy.

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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. Chemical\(^1\) and electrochemical\(^2\) methods have been investigated to regenerate the manganese(III) in situ.

Related compounds including Mn(pic)\(_3\) in DMF [manganese(III)picolinate]\(^3\) and Mn(acac)\(_3\) [manganese(III) acetatoacetonate]\(^4\) are capable of initiating similar reactions.

References

6. Mn(OAc)\(_2\)·4H\(_2\)O and Mn(OAc)\(_3\)·2H\(_2\)O are commercially available.