SYNLETT Spotlight 41

Manganese(III) acetate

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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

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

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