SYNLETT Spotlight 41

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

Manganese(III) acetate

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Introduction

Metal-mediated oxidative radical cyclisations have become a very important method in synthetic chemistry over the last 40 years. 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 γ-lactones in the presence of alkenes. 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-dicarboxyls, have been successfully employed in related reactions, particularly cyclisations, to form 5- and 6-membered rings. The solvent of choice is acetic acid; other solvents (EtOH, CH₃CN, DMSO) tend to give lower yields.

As Mn(OAc)₃ is troublesome to prepare and highly deliquescent, the dihydrate form of the complex [Mn(OAc)₃·2H₂O] is generally used and this is commercially available.

Scheme 1

Abstracts

Mn(OAc)₃ is generally used to form radicals at the α-position of carbonyls and particularly 1,3-dicarboxyls (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.

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

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% 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 \(^{11}\) and electrochemical \(^{12}\) methods have been investigated to regenerate the manganese(III) in situ.

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

References

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