SYNLETT Spotlight 418

**Manganese(III) Acetate**

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Dedicated to my honourable mentor Dr. Utpal Bora

**Introduction**

Manganese(III) acetate \([\text{Mn(OAc)}_3]\)-mediated free-radical reactions have emerged as important synthetic methods. Manganese acetate can be used as an oxidizing and chlorinating agent\(^1\) and in some cases in alkylations\(^1\) and inter- and intramolecular cyclizations.\(^2\) Due to the poor solubility of \(\text{Mn(OAc)}_3\) in common organic solvents, \(\text{Mn(OAc)}_3\)-mediated reactions are often carried out in acetic acid, although other solvents including toluene, alcohols, acetonitrile, dichloromethane and chlorobenzene can be used.\(^3\) \(\text{Mn(OAc)}_3\) promotes the synthesis of many alkaloids,\(^4\) terpenes,\(^5\) and drugs.\(^6\) \(\text{Mn(OAc)}_3\) is commercially available in form of its dehydrate as a brown powder and can be prepared in the laboratory\(^7\) by adding \(\text{KMnO}_4\) to a pre-heated mixture of \(\text{Mn(OAc)}_2\) and glacial acetic acid (Scheme 1). Addition of acetic anhydride to the reaction produces the anhydrous form.\(^8\)

\[ \text{Mn(OAc)}_2 + \text{AcOH} + \text{KMnO}_4 \xrightarrow{110^\circ C} \text{Mn(OAc)}_3 + \text{AcOK} + \text{MnO}_2 \]

**Scheme 1** Preparation of manganese (III) acetate

**Abstracts**

(A) Catalytic amount of manganese acetate in glacial acetic acid oxidizes 3-alkyl-substituted 2,4-pyrrolidinones to their corresponding 3-hydroperoxy derivatives. This procedure leads to a new type of heterocyclic hydroperoxides.\(^9\)

\[
\begin{align*}
\text{R}_1, \text{R}_2 = \text{Ar, Alk} \\
\text{Mn(OAc)}_3 \\
\end{align*}
\]

(B) Manganese acetate-mediated oxidative cyclisation of alkyl substituted 2-[2-(N-arylamino)-2-oxoethyl]malonates yields the corresponding substituted 4,4-bis(ethoxycarbonyl)-3,4-dihydro-2(1H)-quinolinones in good to excellent yield (46–97%).\(^4c\)

\[
\begin{align*}
\text{R}_1 & \quad \text{EtO}_2\text{C} \\
\text{Mn(OAc)}_3 & \quad \text{AcOH, } \Delta \\
\text{up to 99% yield} \\
\end{align*}
\]

(C) Manganese acetate generates aryl radicals or cations when reacted with aryl boronic acids\(^{10a, b}\) or aryl hydrazines\(^{10c}\) preferentially in aromatic solvents (benzene, thiophene) and subsequently leads to the formation of biaryls under microwave,\(^{10a}\) room temperature,\(^{10b}\) and reflux\(^{10c}\) conditions.

\[
\begin{align*}
\text{R}_1 & \quad \text{PhH} \quad \text{PhH} \\
\text{Mn(OAc)}_3 (3 \text{ equiv}) & \quad \text{Mn(OAc)}_3 (3 \text{ equiv}) \\
\end{align*}
\]

(D) When a catalytic amount of manganese acetate is added to a stirred solution of alkyl- or aryl-substituted alcohol and acetic acid, acetylation occurs quantitatively (99% yield) within two hours at reflux.\(^{11}\)
(E) Manganese acetate can be used as an effective and mild oxidizing agent for the regeneration of carbonyl compounds from their corresponding oximes in good yield (86–96%). This reaction condition can tolerate many functional groups, e.g. alkyl and aryl oximes.13

(F) Oxidative ring expansion of substituted 9H-xanthene 1 in the presence of manganese acetate gives 9- or 10-dibenzo[b,f]oxepinocarboylates 2 in good yield. When R1 = Me and R2 = 1-OMe, this reaction gives two regioisomers. Otherwise the reaction is highly regioselective. It was proposed that the process for the formation of the product must include a 1,2-aryl radical rearrangement followed by an oxidative decarboxylation.4b

(G) Under manganese acetate-catalyzed aerobic oxidation conditions in glacial acetic acid, tetronic acid 1 reacts with 1,1-disubstituted alkenes 2 (R1, R2 = Alk, Ar) to yield hydroperoxyethyl peroxylactones 3, while a similar reaction using 3-alkyl-substituted tetronic acid gives stable, crystalline peroxylactone 4 in good to excellent yield.13

(H) Manganese acetate can be employed as an oxidant for the regeneration of 2,3-dichloro-5,6-dicyanoquinone (DDQ) from the corresponding hydroquinone (HDDQ). This DDQ-regeneration technique using manganese acetate (3 equiv) and DDQ (10 mol%), can be applied to the deprotection of p-methoxy benzyl (PMB) ethers.14

(I) Manganese acetate-promoted oxidative free-radical condensation reaction of phosphate ester (dialkylphosphate) with alkynes15 yields the corresponding indenones 1 and direct phosphorylation of arenes6 yields regioselectively dialkylphosphonates 2.

References