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

**Manganese(III) Acetate**

Compiled by Manoj Mondal

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Dedicated to my honourable mentor Dr. Utpal Bora

**Introduction**

Manganese(III) acetate [Mn(OAc)₃]-mediated free-radical reactions have emerged as important synthetic methods. Manganese acetate can be used as an oxidizing and chlorinating agent¹ and in some cases in alkylations¹ and inter- and intramolecular cyclizations.² Due to the poor solubility of Mn(OAc)₃ in common organic solvents, 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 Mn(OAc)₃ promotes the synthesis of many alkaloids,⁴ triterpenes,⁵ and drugs.⁶ Mn(OAc)₃ is commercially available in form of its dehydrate as a brown powder and can be prepared in the laboratory⁷ by adding KMnO₄ to a pre-heated mixture of Mn(OAc)₂ and glacial acetic acid (Scheme 1). Addition of acetic anhydride to the reaction produces the anhydrous form.⁸

**Abstracts**

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

(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

(C) Manganese acetate generates aryl radicals or cations when reacted with aryl boronic acids¹⁰a,b or aryl hydrazines¹⁰c preferentially in aromatic solvents (benzene, thiophene) and subsequently leads to the formation of biaryls under microwave,¹⁰a room temperature,¹⁰b and reflux¹⁰c conditions.

(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

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

SYNLETT 2013, 24, 0137–0138
Advanced online publication: 04.12.2012
DOI: 10.1055/s-0032-1317531; Art ID: ST-2012-V0425-V
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(E) Manganese acetate can be used as an effective and mild oxidizing agent for the regeneration of carboxyl compounds from their corresponding oximes in good yield (86–96%). This reaction condition can tolerate many functional groups, e.g. alkyl and aryl oximes.\textsuperscript{13}

(F) Oxidative ring expansion of substituted 9H-xanthene 1 in the presence of manganese acetate gives 9- or 10-dibenzo[b,f]oxepinocarboxylates 2 in good yield. When $R^1 = \text{Me}$ and $R^2 = 1\text{-OMe}$, 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.\textsuperscript{4b}

(G) Under manganese acetate-catalyzed aerobic oxidation conditions in glacial acetic acid, tetronic acid 1 reacts with 1,1-disubstituted alkenes ($R^1, R^2 = \text{Alk, Ar}$) to yield hydroperoxyethyl peroxylactones 3, while a similar reaction using 3-alkyl-substituted tetrac acid gives stable, crystalline peroxylactone 4 in good to excellent yield.\textsuperscript{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.\textsuperscript{14}

(I) Manganese acetate-promoted oxidative free-radical condensation reaction of phosphate ester (dialkylphosphate) with alkynes\textsuperscript{15} yields the corresponding indenones 1 and direct phosphorylation of arenesc\textsuperscript{6} yields regioselectively dialkylphosphonates 2.

References


