

SYNLETT Spotlight 418

Manganese(III) Acetate

Compiled by Manoj Mondal



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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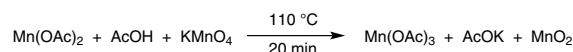
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Dedicated to my honourable mentor Dr. Utpal Bora

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

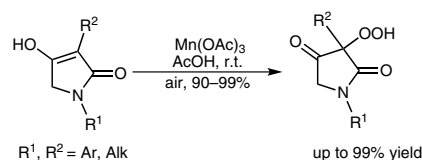
can be used.³ Mn(OAc)₃ promotes the synthesis of many alkaloids,⁴ triterpenes,⁵ and drugs.⁶ Mn(OAc)₃ is commercially available in form of its dehydrate as a brown powder and can be prepared in the laboratory⁷ by adding KMnO₄ to a pre-heated mixture of Mn(OAc)₂ and glacial acetic acid (Scheme 1). Addition of acetic anhydride to the reaction produces the anhydrous form.⁸



Scheme 1 Preparation of manganese (III) acetate

Abstracts

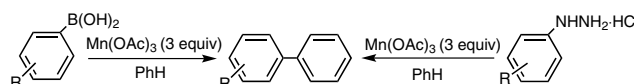
(A) Catalytic amount of manganese acetate in glacial acetic acid oxidizes 3-alkyl-substituted 2,4-pyrrolidinediones to their corresponding 3-hydroperoxy derivatives. This procedure leads to a new type of heterocyclic hydroperoxides.⁹



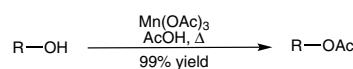
(B) Manganese acetate-mediated oxidative cyclisation of alkyl substituted 2-[2-(*N*-arylamino)-2-oxoethyl]malonates yields the corresponding substituted 4,4-bis(ethoxycarbonyl)-3,4-dihydro-2(1*H*)-quinolinones in good to excellent yield (46–97%).^{4c}



(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.



(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



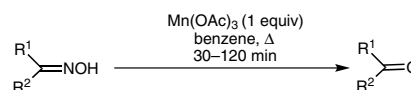
SYNLETT 2013, 24, 0137–0138

Advanced online publication: 04.12.2012

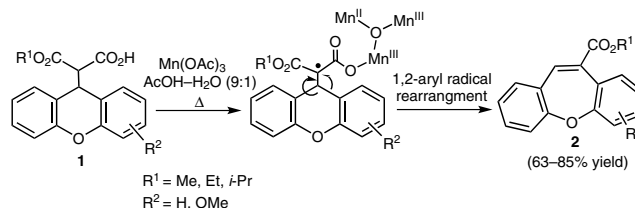
DOI: 10.1055/s-0032-1317531; Art ID: ST-2012-V0425-V

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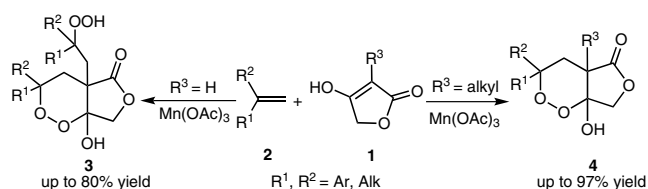
(E) Manganese acetate can be used as an effective and mild oxidizing agent for the regeneration of carbonyl compounds from their corresponding oximes in good yield (86–96%). This reaction condition can tolerate many functional groups, e.g. alkyl and aryl oximes.¹²



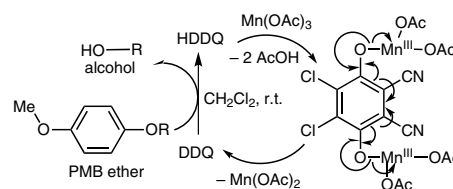
(F) Oxidative ring expansion of substituted 9*H*-xanthenes **1** in the presence of manganese acetate gives 9- or 10-dibenz[*b,f*]oxepincarboxylates **2** in good yield. When R¹ = Me and R² = 1-OMe, this reaction gives two regioisomers. Otherwise the reaction is highly regioselective. It was proposed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



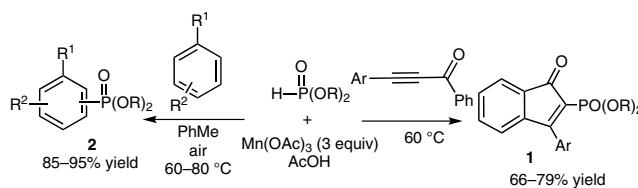
(G) Under manganese acetate-catalyzed aerobic oxidation conditions in glacial acetic acid, tetronic acid **1** reacts with 1,1-disubstituted alkenes **2** (R¹, R² = Alk, Ar) to yield hydroperoxyethyl peroxy lactones **3**, while a similar reaction using 3-alkyl-substituted tetronic acid gives stable,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



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