

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

Manoj Mondal was born in Roing, Arunachal Pradesh, India, in 1986. He received his MSc degree in Organic Chemistry in 2010 from Dibrugarh University. He then joined Dr. U. Bora's research group at Dibrugarh University to pursue his PhD studies. His research interests focus on the synthesis of palladium- and copper-based catalysts for carbon-carbon, carbon-heteroatom bond-formation reactions.

Department of Chemistry, Dibrugarh University, Dibrugarh 786004, India

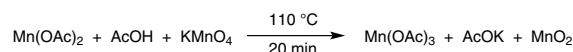
E-mail: manojmondal@gmail.com

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

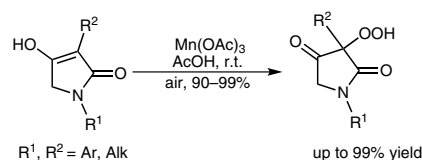
can be used.³ Mn(OAc)₃ promotes the synthesis of many alkaloids,⁴ triterpenes,⁵ and drugs.⁶ Mn(OAc)₃ is commercially available in form of its dehydrate as a brown powder and can be prepared in the laboratory⁷ by adding KMnO₄ to a pre-heated mixture of Mn(OAc)₂ and glacial acetic acid (Scheme 1). Addition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



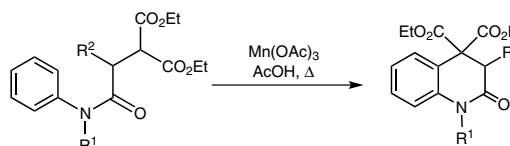
Scheme 1 Preparation of manganese (III) acetate

Abstracts

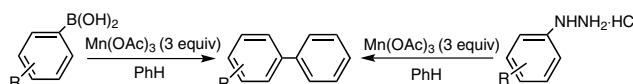
(A) Catalytic amount of manganese acetate in glacial acetic acid oxidizes 3-alkyl-substituted 2,4-pyrrolidinediones to their corresponding 3-hydroperoxy derivatives. This procedure leads to a new type of heterocyclic hydroperoxides.⁹



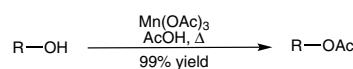
(B) Manganese acetate-mediated oxidative cyclisation of alkyl substituted 2-[2-(*N*-arylamino)-2-oxoethyl]malonates yields the corresponding substituted 4,4-bis(ethoxycarbonyl)-3,4-dihydro-2(1*H*)-quinolinones in good to excellent yield (46–97%).^{4c}



(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



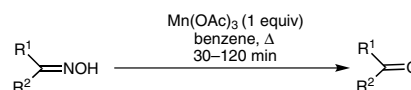
SYNLETT 2013, 24, 0137–0138

Advanced online publication: 04.12.2012

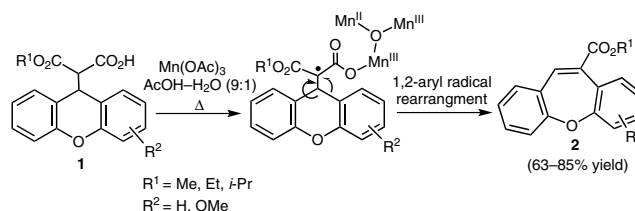
DOI: 10.1055/s-0032-1317531; Art ID: ST-2012-V0425-V

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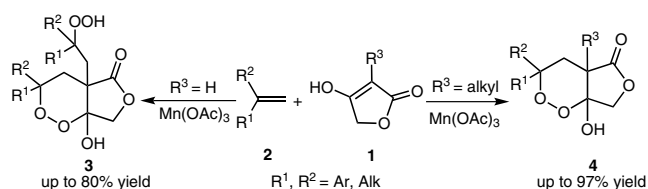
(E) Manganese acetate can be used as an effective and mild oxidizing agent for the regeneration of carbonyl compounds from their corresponding oximes in good yield (86–96%). This reaction condition can tolerate many functional groups, e.g. alkyl and aryl oximes.¹²



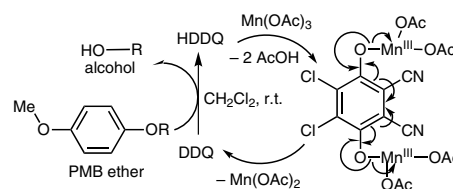
(F) Oxidative ring expansion of substituted 9H-xanthene **1** in the presence of manganese acetate gives 9- or 10-dibenz[*b,f*]oxepincarboxylates **2** in good yield. When R¹ = Me and R² = 1-OMe, this reaction gives two regioisomers. Otherwise the reaction is highly regioselective. It was proposed that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



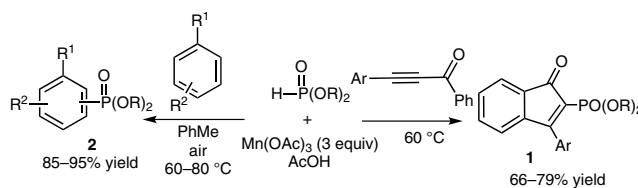
(G) Under manganese acetate-catalyzed aerobic oxidation conditions in glacial acetic acid, tetric acid **1** reacts with 1,1-disubstituted alkenes **2** (R¹, R² = Alk, Ar) to yield hydroperoxyethyl peroxy lactones **3**, while a similar reaction using 3-alkyl-substituted tetric acid gives stable, crystalline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