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Spotlight 418

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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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 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 laboratory\(^7\) by adding KMnO\(_4\) 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-oxyethyl]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 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.\(^11\)

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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.\(^{13}\)

(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 \(R^1 = \text{Me}\) and \(R^2 = 1\)-OMe, this reaction gives two regioisomers. Otherwise the reaction is highly regioselective. It was proposed that 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 3 reacts with 1,1-disubstituted alkenes \((R^1, R^2 = \text{Alk}, \text{Ar})\) to yield hydroperoxyethyl peroxylactones 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 alkynes yields the corresponding indenones 1 and direct phosphorylation of arenes yields regioselectively dialkylphosphonates 2.

References