

# 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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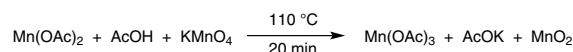
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Dedicated to my honourable mentor Dr. Utpal Bora

### Introduction

Manganese(III) acetate [Mn(OAc)<sub>3</sub>]-mediated free-radical reactions have emerged as important synthetic methods. Manganese acetate can be used as an oxidizing and chlorinating agent<sup>1</sup> and in some cases in alkylations<sup>1</sup> and inter- and intramolecular cyclizations.<sup>2</sup> Due to the poor solubility of Mn(OAc)<sub>3</sub> in common organic solvents, Mn(OAc)<sub>3</sub>-mediated reactions are often carried out in acetic acid, although other solvents including toluene, alcohols, acetonitrile, dichloromethane and chlorobenzene

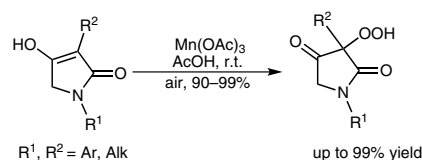
can be used.<sup>3</sup> Mn(OAc)<sub>3</sub> promotes the synthesis of many alkaloids,<sup>4</sup> triterpenes,<sup>5</sup> and drugs.<sup>6</sup> Mn(OAc)<sub>3</sub> is commercially available in form of its dehydrate as a brown powder and can be prepared in the laboratory<sup>7</sup> by adding KMnO<sub>4</sub> to a pre-heated mixture of Mn(OAc)<sub>2</sub> and glacial acetic acid (Scheme 1). Addition of acetic anhydride to the reaction produces the anhydrous form.<sup>8</sup>



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

### Abstracts

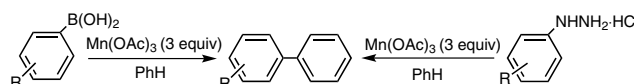
(A) Catalytic amount of manganese acetate in glacial acetic acid oxidizes 3-alkyl-substituted 2,4-pyrrolidinediones to their corresponding 3-hydroperoxy derivatives. This procedure leads to a new type of heterocyclic hydroperoxides.<sup>9</sup>



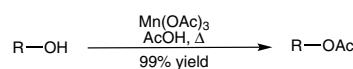
(B) Manganese acetate-mediated oxidative cyclisation of alkyl substituted 2-[2-(*N*-arylamino)-2-oxoethyl]malonates yields the corresponding substituted 4,4-bis(ethoxycarbonyl)-3,4-dihydro-2(1*H*)-quinolinones in good to excellent yield (46–97%).<sup>4c</sup>



(C) Manganese acetate generates aryl radicals or cations when reacted with aryl boronic acids<sup>10a,b</sup> or aryl hydrazines<sup>10c</sup> preferentially in aromatic solvents (benzene, thiophene) and subsequently leads to the formation of biaryls under microwave,<sup>10a</sup> room temperature,<sup>10b</sup> and reflux<sup>10c</sup> 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.<sup>11</sup>



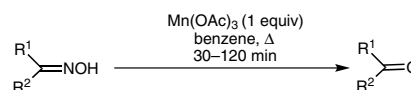
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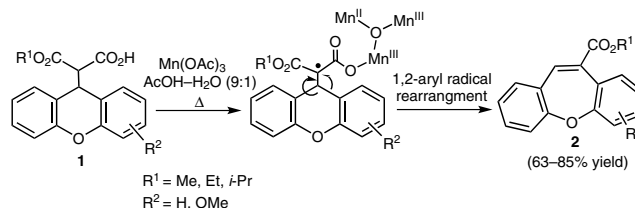
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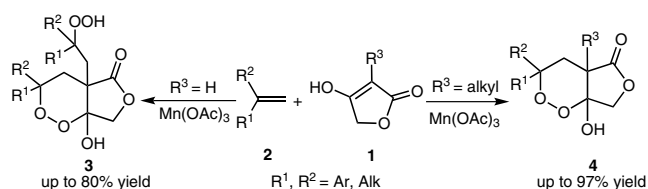
(E) Manganese acetate can be used as an effective and mild oxidizing agent for the regeneration of carbonyl compounds from their corresponding oximes in good yield (86–96%). This reaction condition can tolerate many functional groups, e.g. alkyl and aryl oximes.<sup>12</sup>



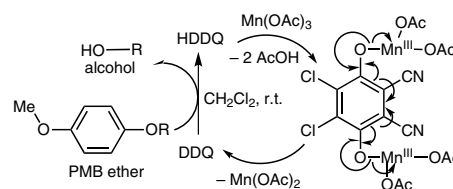
(F) Oxidative ring expansion of substituted 9*H*-xanthenes **1** in the presence of manganese acetate gives 9- or 10-dibenz[*b,f*]oxepincarboxylates **2** in good yield. When R<sup>1</sup> = Me and R<sup>2</sup> = 1-OMe, this reaction gives two regioisomers. Otherwise the reaction is highly regioselective. 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.<sup>4b</sup>



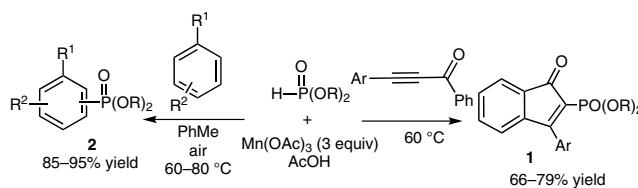
(G) Under manganese acetate-catalyzed aerobic oxidation conditions in glacial acetic acid, tetronic acid **1** reacts with 1,1-disubstituted alkenes **2** (R<sup>1</sup>, R<sup>2</sup> = Alk, Ar) to yield hydroperoxyethyl peroxy lactones **3**, while a similar reaction using 3-alkyl-substituted tetronic acid gives stable, crystalline peroxy lactone **4** in good to excellent yield.<sup>13</sup>



(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.<sup>14</sup>



(I) Manganese acetate-promoted oxidative free-radical condensation reaction of phosphate ester (dialkylphosphate) with alkynes<sup>15</sup> yields the corresponding indenones **1** and direct phosphorylation of arenes<sup>6</sup> yields regioselectively dialkylphosphonates **2**.



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