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Manganese triacetate oxidation of methyl 1-hydroxy-2-naphthalene carboxylates

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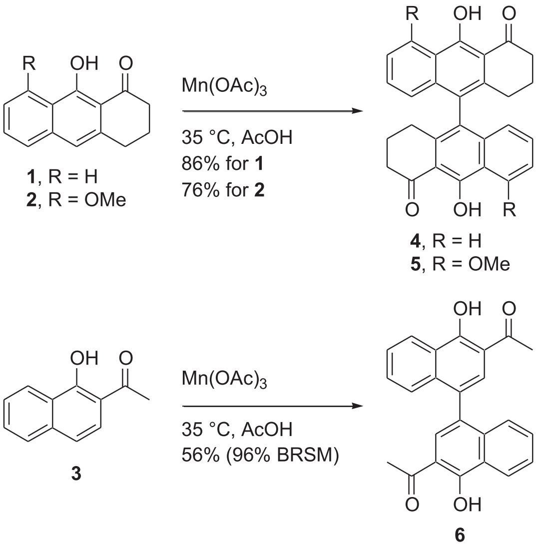
ABSTRACT

Manganese-triacetate mediated oxidation of 1-hydroxy-2-napthalene carboxylates in benzene under anhydrous conditions delivers the dimerized product. However, acetoxylation on the *ortho*- or *para*-position, or oxidation to quinones occurs on the 1-hydroxy-3-substituted 2-napthalene carboxylates depending on the nature of the substituents when the reaction is carried out in a mixture of acetic acid/acetonitrile.

Introduction

Manganese triacetate, a one-electron oxidant, has attracted the attention of many research groups over the past decade due to its multiple synthetic applications.[1] Manganese triacetate has been particularly valuable to oxidize acetic acid and β-dicarbonyl compounds to the corresponding carbon-centered radical adding to alkenes.[2] The manganese complex has also been useful to α′-acetoxylate cyclic α,β-unsaturated ketones.[3] This α′-acetoxylation has been reported in acetic acid or in refluxing benzene. A mechanism for this reaction was suggested to undergo an acetate transfer from a metal enolate. Snider reported a manganese triacetate-mediated oxidative coupling of hydroxyanthracenone **1** when heating acetic acid to 35 °C for 24 h to deliver dimeric anthracenone **4** in good yield, Scheme 1.[4] Manganese triacetate-mediated oxidative homocoupling of the hydroxyanthracenone is simple and does not require any functionalization of the scaffold. There are some biologically active dimeric natural products that possess a bis-hydroxyanthracenone scaffold.[5] Because of our interest in this type of natural products, we investigated this manganese triacetate mediated dimerization with other substrates. We observed that hydroxymethoxyanthracenones **1** and **2**, and 2-acetyl-1-naphthol (**3**) underwent dimerization employing the same reaction conditions, Scheme 1. However, when the substrate was methyl 1-hydroxy-2-naphthalenecarboxylate (**7a**) a mixture of dimerized and acetoxylated products (**8a** and **9**, respectively) were obtained utilizing Snider's conditions, entry 1, Table 1. Acetoxylation on the para position occurred probably through a Wessely oxidation followed by rearrangement.[6]



Scheme 1. Dimerization of hydroxyanthracenones and acetylhydroxynaphthalene.

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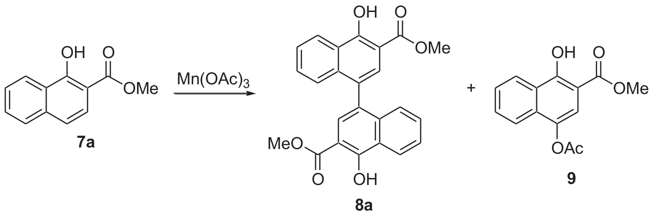
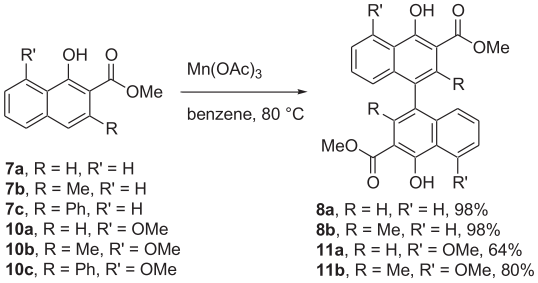
Table 1
Reaction conditions for Manganese-mediated oxidation of methyl 1-hydroxy-2-naphthalene carboxylate.



Entry	Mn(III) (equiv)	Time (h)	Solvent	Temp (°C)	Ratio[a] **8a**/**9**	Yield (%)
1	2	24	AcOH	35	25:75	92
2	2	3	AcOH:CH_3CN, 1:1	35	24:76	92
3	2	6	AcOH:CH_3CN, 1:1	35	15:85	90
4	3	12	AcOH:CH_3CN, 1:1	35	–:100	89
5	2	3	AcOH:CH_3CN, 1:1	80	50:50	88
6	2	12	AcOH:CH_3CN, 1:1	80	–:100	89
7	2	4	Benzene	80	100:–	97
8	1.25	4	Benzene	80	100:–	98

[a] Ratio determined by ^{1}H NMR spectra of crude product.

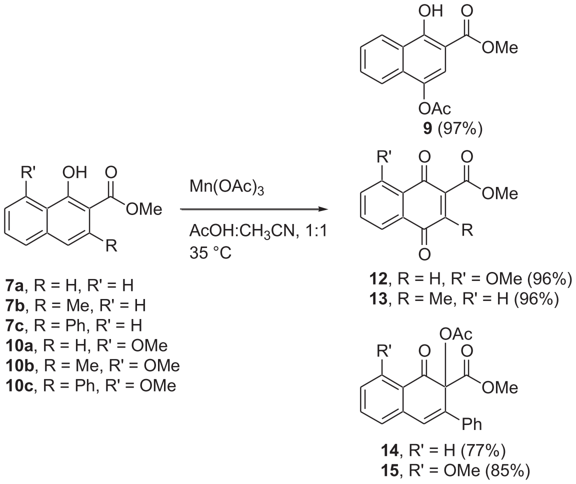


Scheme 2. Dimerization of methyl 1-hydroxy-2-naphthalene-carboxylate.

Results and discussion

This is the first observation of a Wessely acetoxylation of aromatics with manganese triacetate. Adding an equal amount of acetic acid and acetonitrile gave similar results in less time (entry 2). Increasing reaction time and the amount of manganese complex resulted in complete acetoxylation of the naphthol exclusively on the *para*-position to the hydroxyl group (entries 3 and 4). Increasing the reaction temperature and three hours of stirring delivered an equal mixture of dimer and acetoxylation products (entry 5). Again, longer reaction times at high temperature gave only acetoxylation product when the reaction was run for twelve hours (entry 6). Interestingly, when the reaction was carried out in benzene under anhydrous conditions at high temperature, only dimerization occurred even with only a slight excess of metal complex (entries 7 and 8).

Having found reaction conditions that favored dimerization over acetoxylation of the hydroxynaphthalene carboxylate, we applied these to the dimerization of 3-substituted 1-hydroxynapthalenecarboxylates **7a**–**c** and 8-methoxy-1-hydroxynapthalenecarboxylates **10a**–**c**, Scheme 2. Dimerization occurred in excellent to good yield when substrates lacked a substituent on C-3 (dimers **7a** and **10a**). Dimerization also occurred in excellent and good yields when the 3-substituent was a methyl group (dimers **8b** and **11b**). However, no reaction was observed when the substituent was a phenyl group (**7c** and **10c**). Lack of reactivity towards dimerization of the 3-phenyl substituted hydroxynaphthalenecarboxylates is probably because of steric effects.



Scheme 3. Oxidation of methyl 1-hydroxy-2-naphthalene-carboxylates in AcOH: CH_3CN.

We then explored the manganese triacetate oxidation in acetic acid/acetonitrile with the same substrates **7a**–**c** and **10a**–**c**, Scheme 3. Interestingly, employing this solvent system, the product obtained depended on the substituent on C-3. Acetoxylation occurred on the para position when naphthalenecarboxylate lacked a substituents on C-3 and **8** (acetoxynaphthalene **9**). Oxidation to *p*-quinones occurred when the naphthalenecarboxylate possessed an 8-methoxy group (*p*-quinone **12**) or a 3-methyl group (*p*-quinone **13**). An inseparable mixture of products was obtained for carboxylate **10b**. Wessely acetoxylation, solely on carbon-2, occurred for the sterically hindered 3-phenylnaphthalenecarboxylates **7c** and **10c** (products **14** and **15**).

Conclusions

In summary, we investigated the Mn-triacetate oxidation of 1-hydroxy-2-napthalene carboxylates. Dimerization occurred selectively employing anhydrous conditions in benzene, except for the 3-phenyl derivatives. Oxidation employing acetic acid-acetonitrile gave Wessely acetoxylated products or quinones depending on the substituents of the napthalenecarboxylate. This oxidative homo-

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coupling reaction is simple and requires no functionalization on the aromatic system.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2017.05.028.

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