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A New and Facile Method for the Direct Preparation of α-Hydroxycarboxylic Acid Esters from α,β-Unsaturated Carboxylic Acid Esters with Molecular Oxygen and Phenylsilane Catalyzed by Bis(dipivaloylmethanato)manganese(II) Complex

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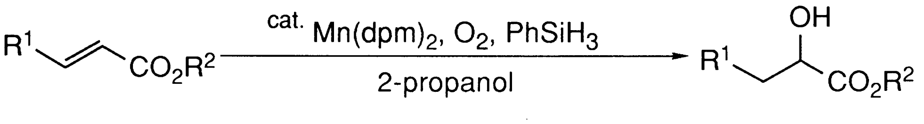
In the presence of a catalytic amount of bis(dipivaloylmethanato)manganese(II) complex, the oxygenation of benzyl crotonate with molecular oxygen and phenylsilane proceeds smoothly under a mild condition to give benzyl 2-hydroxybutyrate in high yield. The reaction provides a new and convenient method for the direct preparation of various α-hydroxycarboxylic acid esters starting from α,β-unsaturated carboxylic acid esters. The influence of substituents of olefins on regioselectivity is also studied.

Derivatives of α-hydroxycarboxylic acid esters are one of the useful intermediates for the synthesis of α-ketocarboxylic acid esters[1)] and heterocyclic compounds,[2)] and many preparative methods have been reported. For example, α-hydroxycarboxylic acid esters were produced by the hydrolysis of α-halocarboxylic acid esters,[3)] by the rearrangement of α-ketoacetals,[4)] or by the oxidation of ketene silyl acetals.[5)] However, little work have been reported on direct preparation of α-hydroxycarboxylic acid ester from α,β-unsaturated carboxylic acid ester. Previously, we have reported a cobalt(II) catalyzed peroxygenation reaction of α,β-unsaturated carboxylic acid esters and it was succesfully extended to the formation of α-hydroxycarboxylic acid esters by the subsequent reduction of the produced α-triethylsilyldioxy carboxylic acid esters.[6)] During the course of our continuing study, our interests have been focused on direct preparation of α-hydroxycarboxylic acid esters from α,β-unsaturated carboxylic acid esters. And now, it was found that the oxygenation of α,β-unsaturated carboxylic acid esters with O_2 and $PhSiH_3$ proceeds smoothly in the presence of bis(dipivaloylmethanato)manganese(II) ($Mn(dpm)_2$) to afford the corresponding α-hydroxycarboxylic acid esters in high yields under mild condition.

In this communication, we would like to describe a convenient method for the preparation of α-hydroxycarboxylic acid esters from α,β-unsaturated carboxylic acid esters by one-pot procedure.



Scheme 1.

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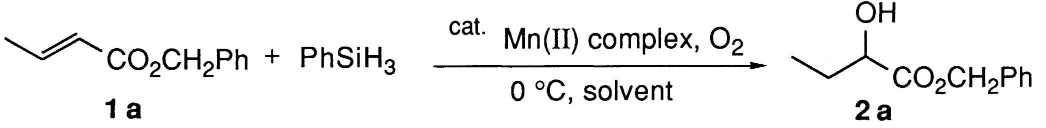
In the first place, the effect of ligands in Mn(II) complex catalysts was examined by taking the formation of benzyl 2-hydroxybutyrate (**2a**) from benzyl crotonate (**1a**) as a model reaction and it was found that Mn(dpm)$_2$ is effectively employed as catalyst (Table 1). Also, Mn(acac)$_2$ showed moderate catalytic activity.

In addition, a remarkable solvent effect was observed in the above reaction on improvement of yields of **2a**. As shown in Table 1, when the reaction was carried out in primary or secondary alcohol, **1a** was smoothly converted into **2a** in high yield (Entries 2-4). However, in case of tertiary alcohol (t-butyl alcohol and t-pentyl alcohol) or non-alcoholic solvents (THF), the reaction proceeded very slowly and yield of **2a** was low.

Table 1. Hydration of Benzyl crotonate

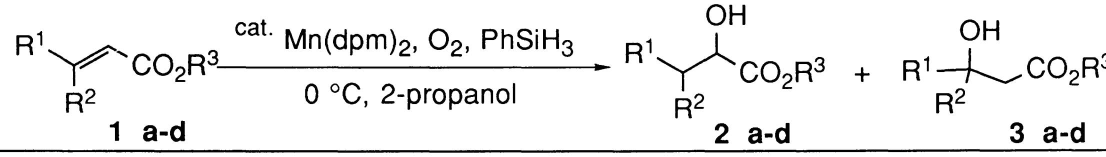


Entry	Mn(II) complex	Solvent	Time /h	Conv. of **1a** /%[a]	Yield of **2a** /%[a]
1	Mn(acac)$_2$[b]	2-propanol	3	84	62
2	Mn(dpm)$_2$[c]	2-propanol	3	100	91
3	Mn(dpm)$_2$[c]	ethanol	3	92	84
4	Mn(dpm)$_2$[c]	1-butanol	3	93	83

a) Determined by GC. b) Reaction condition; **1a** 2.0 mmol, Mn(acac)$_2$ 0.1 mmol, PhSiH$_3$ 4.0 mmol, solvent 10 ml, 1 atm. O$_2$. c) Reaction conditions; **1a** 2.0 mmol, Mn(dpm)$_2$ 0.04 mmol, PhSiH$_3$ 4.0 mmol, solvent 10 ml, 1 atm. O$_2$.

In the next stage, the present reaction was applied to α,β-unsaturated carboxylic acid esters having methyl or phenyl groups on β-position (**1b**, **1c**, and **1d**) (see Table 2). When benzyl β,β-dimethylacrylate (**1b**) was treated with O$_2$ and phenylsilane in the presence of Mn(dpm)$_2$ catalyst, β-hydroxycarboxylic acid ester (**3b**) was obtained in 12% yield along with α-hydroxycarboxylic acis ester (**2b**) in 24% yield. Further, in the cases of **1c** and **1d**, β-hydroxycarboxylic acid esters (**3c** and **3d**) were obtained as main products (65% and 73% yields, respectively). Based on these results, it is noted that the regioselectivity of the above reaction is strongly influenced by the substituents on β-position of α,β-unsaturated carboxylic acid esters. Accordingly, it was

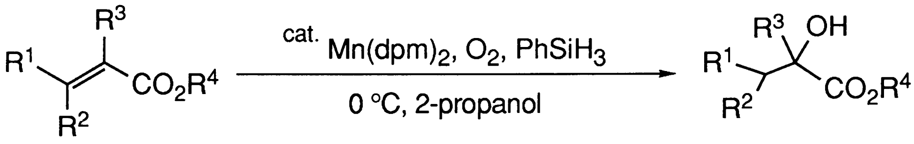
Table 2 . Effect of Subsituents on β-position [a]

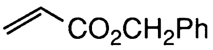
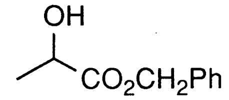
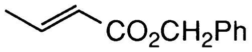
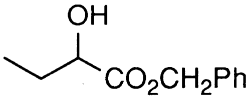
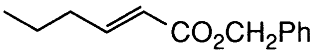
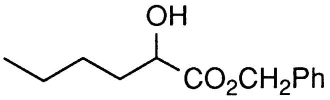
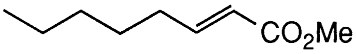
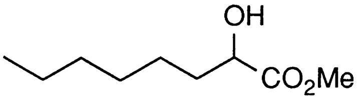
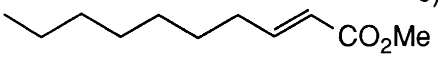
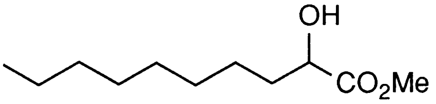
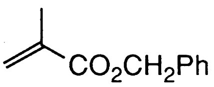
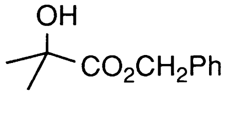
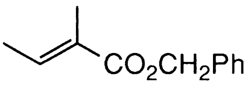
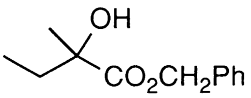
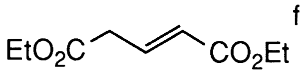
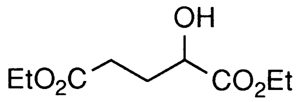
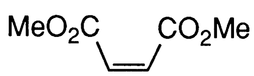
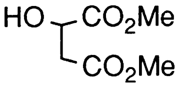
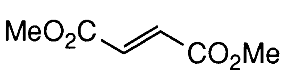
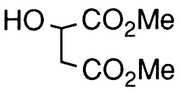


Entry	R^1	R^2	R^3		Time /h	Conv. of **1** /%[b]	Yield of **2** /%[b]	Yield of **3** /%[b]
1	CH$_3$	H	CH$_2$Ph	(**a**)	3	100	91	0
2	CH$_3$	CH$_3$	CH$_2$Ph	(**b**)	12	56	24	12
3	Ph	H	Et	(**c**)	15	100	11	65
4	Ph	Ph	Et	(**d**)	15	100	0	73

a) Reaction conditions; substrate 2.0 mmol, Mn(dpm)$_2$ 0.04 mmol, PhSiH$_3$ 4.0 mmol, 2-propanol 10 ml ,1 atm. O$_2$.
b) Isolated yields.

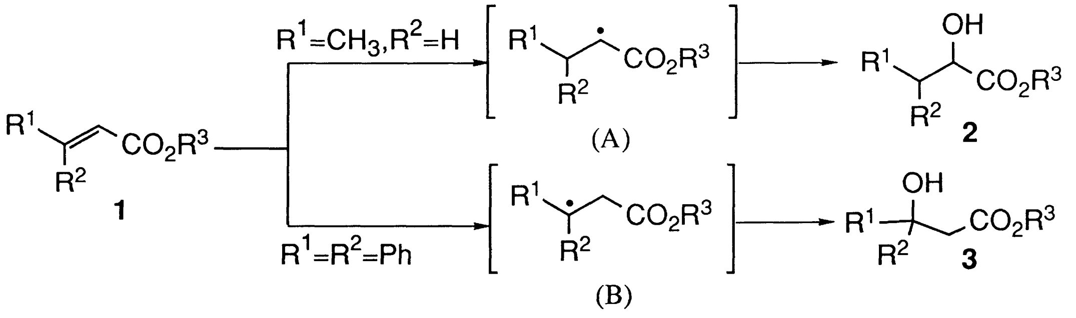
Table 3. Preparation of Various α-Hydoxycarboxylic Acid Esters [a)]



Entry	Substrate	Time /h	Product [b,c,d)]	Yield /%
1		2		91
2		3		91
3	 e)	3		86
4	 e)	5		94
5	 e)	3		84
6		1.5		92
7		2		94
8	 f)	4		82
9	 f)	6		78
10	 g)	4		76

a) Reaction conditions; substrate 2.0 mmol, $Mn(dpm)_2$ 0.04mmol, $PhSiH_3$ 4.0 mmol, 2-propanol 10 ml, 0 °C, 1 atm. O_2. b) Isolated yield. c) Entries 1 to 8, no β-hydroxycarboxylic acid ester was formed. d) All products gave satisfactory ^{1}H-NMR and IR spectra. e) $PhSiH_3$ 3.0 mmol, 2-propanol 2 ml. f) Solvent; ethanol 5 ml.
g) Solvent; ethanol 3.5 ml and 1,2-dichloroethane 1.5 ml.

assumed that the present reaction would proceed *via* a radical spieces (A or B) as a reaction intermediate (Scheme 2). Stabilized radical carbon atoms on the above intermediates (A or B) are oxygenated to give the corresponding hydroxycarboxylic acid esters.



Scheme 2.

Next, the hydration of several aliphatic α,β-unsaturated carboxylic acid esters was tried according to the above procedure (Table 3). In Entries 1 to 8, the reaction proceeded smoothly and the corresponding α-hydroxycarboxylic acid esters were obtained regioselectively in high yields. In addtion, it is noted that only malic acid ester resulted in good yield starting from both fumaric acid ester and maleic acid ester.

A typical procedure is described for the preparation of benzyl 2-hydroxybutyrate; to a solution of benzyl crotonate (352 mg, 2.0 mmol) and $Mn(dpm)_2$ (16.8 mg, 0.04 mmol) in 2-propanol (10 ml) was added phenylsilane (432 mg, 4.0 mmol) at 0 °C under an oxygen atmosphere. After being stirred for 3 h at 0 °C, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ solution (5 ml) at 0 °C. Then, the organic materials were extracted with ethyl acetate and the combined organic extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC (silicagel, hexane : ethyl acetate = 3 : 1) to give benzyl 2-hydroxybutyrate (353 mg, 91%).

Thus, it is noted that various aliphatic α-hydroxycarboxylic acid esters are readily produced regioselectively in high yields directly from α,β-unsaturated carboxylic acid esters on the treatment with molecular oxygen and phenylsilane in the presence of a catalytic amount of $Mn(dpm)_2$.

References

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