

A facile catalytic oxidation of activated hydrocarbons to the carbonyl functionality mediated by Mn(II) complexes

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Abstract

Selective oxidation of activated hydrocarbons to the corresponding carbonyl functionality was achieved with good to high material yields using novel camphor-derived ligands mediated with Mn(II) as catalyst. In general, the reaction proceeds smoothly with 5 mol% of catalyst and 2.0 eq. of *t*-BuOOH as oxidant in CH₂Cl₂ in 5–30 min. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxidation of activated hydrocarbons to the corresponding oxygenated functionality constitutes one of the most fundamental transformations in organic synthesis [1–9]. The corresponding ynols, ynones, enols, enones, arylketones and lactones are of synthetically valuable intermediates for further elaboration. Conventional approaches for the oxidations require the use of stoichiometric amounts of transition metal complexes such as chromium reagents and manganese reagents under homogeneous/heterogeneous conditions. Tedious work up procedures and the generation of environmentally hazardous metal residues are among the main disadvantages. The catalytic methods for the benzylic/allylic C–H oxidation is a subject of recent interest [10–23]. The transformation of hydrocarbons through the action of metal com-

plexes have proved to be effective, particularly when the complexes act as catalysts [24,25]. Chromium complexes derivatives are strong oxidants which are used for benzylic oxidation [26–31]. The use of manganese complexes for the oxidation of activated hydrocarbons has been studied [32,33]. On the other hand, the use of (salen)manganese(III) complexes for asymmetric oxidation have been reported with success [34–36]. The (salen)manganese(III) complexes have been found to catalyze oxidation of the hydrocarbons to give a hydroxy functionality [37]. These reactions have been proposed via a radical intermediate. The use of (salen)manganese(III) complex as catalyst to effect the oxidation of benzylic C–H bond to the carbonyl group in the presence of PhIO was reported recently [38]. In continuation with our research interests in the asymmetric allylic oxidation mediated with chiral catalyst, we have synthesized several camphor-derived ligands and screened various metal reagents in the presence of oxidant. Herein we wish to disclose the Mn(II)-mediated catalyst to accelerate

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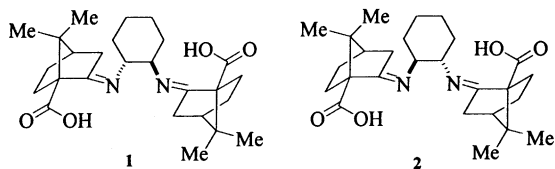
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the oxidation of various activated hydrocarbons to the corresponding carbonyl groups using *t*-BuOOH as terminal oxidant. In general, good to high material yields of the products can be obtained in 5–30 min under mild reaction conditions.

2. Results and discussion

The novel camphor-derived dimerized ligands **1** and **2** were prepared from the condensation of (+)-ketopinic acid with *trans*-1,2-diaminocyclohexane in refluxing CHCl₃ for 36 h. The diamine **1** and **2** were isolated in 45 and 31%, respectively, after careful flash column chromatography. The structures of these two ligands were assigned by ¹H-, ¹³C-NMR and HRMS analyses and the absolute stereochemistry of **1** was further confirmed by single crystal X-ray analysis. The catalyst can be easily prepared by treatment of the ligand with 1.0 eq. of Mn(OAc)₂·4H₂O in CHCl₃ to give dark brownish Mn complexes which can be used directly.



We first examined the oxidation reaction with indan as a probe substrate to determine its feasibility. Indan was smoothly oxidized to 1-indanone in 92% isolated yield upon exposure to the reaction conditions (5 mol% of catalyst **1**, Mn(OAc)₂·4H₂O in CH₂Cl₂ at 0°C) in 5 min while the blank reaction takes 60 min to give only trace amount of product (entries 1 and 2). The use of 50 mol% of Mn(OAc)₂·4H₂O in the absence of ligand gave similar result (entry 3). This indicates that the metal complexes play a prime role in accelerating the reaction rate. Similar result was obtained by the use of the diastereomeric catalyst **2**, Mn(OAc)₂·4H₂O under the same reaction conditions (entry 4). Due to the solubility problems of the catalyst, limited solvents were studied and significant solvent effects were observed (entries 5–7). The use of CH₃CN as solvent affords the desired product with 70% chemical yield. When the reaction was carried out in MeOH to give 67% material yield while the

use of THF as solvent the desired product was isolated in only 28% yield after 12 h at RT. The CH₂Cl₂ turns out to be the solvent of choice for this reaction. Various oxidants were also investigated. Treatment of indan with the catalyst in the presence of cumene hydroperoxide (CMHP) provided 1-indanone in 42% chemical yield (entry 8). The use of *m*-CPBA failed to give the desired product (entry 9). In general, the use of inorganic oxidants resulting in low chemical yields (entries 10–13). Trial of the reaction with chromium salt such as CrCl₃·6H₂O oxidize indan to 1-indanone in 92% yield for 24 h at RT (entry 14). However, similar result was observed in the absence of ligand **1** (entry 15). This indicates that ligand **1** was not severely involved in the benzylic C–H oxidation in the CrCl₃·6H₂O/TBHP system (Table 1).

The new oxidation system is found to be of generally versatile with various benzylic substrates under the optimum reaction conditions. Toluene was oxidized readily to benzaldehyde by this catalytic system (Table 2, entry 1). Propylbenzene was oxidized to propiophenone with 91% chemical yield in 10 min (entry 2). Indene was oxidized to 1*H*-inden-1-ol as the major product in 71% yield with 2.0 eq. of oxidant under this reaction conditions (entry 3). When 1*H*-inden-1-ol was subject to the same reaction conditions for 210 min no sign of the desired product was produced (entry 4). The α-tetralone was readily obtained from the corresponding 1,2,3,4-tetrahydronaphthalene (entry 5). The benzyl ethers such as phthalan and isochroman were oxidized to phthalide (76%) and isochroman-1-one (82%), respectively (entries 6 and 8). Treatment of phthalan with excess *t*-BuOOH (5.0 eq.) in attempting to give phthalic anhydride failed and phthalide was isolated instead (entry 7). Fluorene and 9,10-dihydroanthracene were oxidized to the corresponding 9-fluorenone and anthraquinone at relatively low reaction rate with moderate chemical yields (entries 9 and 10). The oxidation of allylic hydrocarbons were also investigated. The cyclohexene was oxidized to 2-cyclohexen-1-one with high chemical yield (entry 11). 1-Phenyl-1-cyclohexene was converted to 3-phenylcyclohex-2-enol in 67% chemical yield in 30 min (entry 12). The resulting enol can be further oxidized to 3-phenylcyclohex-2-enone under prolonged reaction time in almost quantitative yield (entry 13). *Trans*-stilbene and styrene were oxidized to benzaldehyde easily (entries 14 and 15).

Table 1
Oxidation of indan with chiral catalyst^a

Run	Ligand ^b (mol%)	Metal	Oxidant ^c	Solvent	<i>t</i> (min)	1-Indanone ^d (%)
1	1 (5)	Mn(OAc) ₂ ·4H ₂ O	TBHP	CH ₂ Cl ₂	5	92
2	None	Mn(OAc) ₂ ·4H ₂ O	TBHP	CH ₂ Cl ₂	60	<5
3	None	Mn(OAc) ₂ ·4H ₂ O ^e	TBHP	CH ₂ Cl ₂	120	<5
4	2 (5)	Mn(OAc) ₂ ·4H ₂ O	TBHP	CH ₂ Cl ₂	5	91
5	1 (5)	Mn(OAc) ₂ ·4H ₂ O	TBHP	CH ₃ CN	30	70
6	1 (5)	Mn(OAc) ₂ ·4H ₂ O	TBHP	MeOH	30	67
7	1 (5)	Mn(OAc) ₂ ·4H ₂ O	TBHP	THF	720	28
8	1 (5)	Mn(OAc) ₂ ·4H ₂ O	CMHP ^f	CH ₂ Cl ₂	60	42
9	1 (5)	Mn(OAc) ₂ ·4H ₂ O	<i>m</i> -CPBA	CH ₂ Cl ₂	60	0
10	1 (5)	Mn(OAc) ₂ ·4H ₂ O	H ₂ O ₂ (35%)	CH ₂ Cl ₂	120	20
11	1 (5)	Mn(OAc) ₂ ·4H ₂ O	Oxone	CH ₂ Cl ₂	120	10
12	1 (5)	Mn(OAc) ₂ ·4H ₂ O	H ₅ IO ₆	CH ₂ Cl ₂	120	30
13	1 (5)	Mn(OAc) ₂ ·4H ₂ O	aq. NaOCl	CH ₂ Cl ₂	60	0
14	1 (5)	CrCl ₃ ·6H ₂ O	TBHP	CH ₂ Cl ₂	1440	92
15	None	CrCl ₃ ·6H ₂ O	TBHP	CH ₂ Cl ₂	1440	89

^a Unless specific indicated, all reactions were performed at 0°C. The catalyst was prepared by treatment of chiral ligand **1** or **2** with Mn(OAc)₂·4H₂O (1.0 eq.) in refluxing CHCl₃ for 12 h. The solvent was removed in vacuo and dry under high vacuum system to provide dark brownish solid which was used directly.

^b The chiral non-racemic ligands of **1** and **2** were used.

^c 2.0 eq. of oxidant was used for each run.

^d Isolated yield.

^e 50 mol% of Mn(OAc)₂·4H₂O was used in the blank reaction.

^f Cumene hydroperoxide.

Table 2
Reaction of various activated hydrocarbons with the catalytic oxidation system^a

Run	Substrate	<i>t</i> (min)	Product	Chemical yield ^b (%)
1	Toluene	10	Benzaldehyde	>85
2	Propylbenzene	10	Propiophenone	91
3	Indene	30	1 <i>H</i> -inden-1-ol ^c	71
4	1 <i>H</i> -inden-1-ol	210	1 <i>H</i> -inden-1-ol	0
5	1,2,3,4-Tetrahydronaphthalene	10	α-Tetralone	88
6	Phthalan	20	Phthalide	76
7	Phthalan	20	Phthalide ^d	76
8	Isochroman	15	Isochroman-1-one	82
9	Fluorene	120	9-Fluorenone	63
10	9,10-Dihydroanthracene	120	Anthraquinone	52
11	Cyclohexene	20	2-Cyclohexen-1-one	>85
12	1-Phenyl-1-cyclohexene	30	3-Phenylcyclohex-2-enol ^c	67
13	1-Phenyl-1-cyclohexene	720	3-Phenylcyclohex-2-enone	67
14	<i>Trans</i> -stilbene	10	Benzaldehyde	>90
15	Styrene	10	Benzaldehyde	>90

^a Unless specific indicated, all reactions were performed at 0°C using the stock catalyst (5 mol% of **1**, Mn(OAc)₂·4H₂O), *t*-BuOOH (2.0 eq.) in CH₂Cl₂.

^b Isolated yield.

^c Enantiomeric excess not determined.

^d 5.0 eq. of *t*-BuOOH was used.

The mechanism for this transformation is unclear at this moment. The ligand manganese-oxo complexes have been considered to be the active species and the reaction proceeds via a radical intermediate for the oxidation [38–42].

In summary, the present method represents an alternative and efficient catalytic system for the oxidation of toluene, alkylbenzene, cyclic benzyl ethers and allylic hydrocarbons to the corresponding carbonyl functionality. The dimerized ligands **1** and **2** are easily prepared and the oxidation reaction proceeds smoothly at 0°C at relative short reaction period. The investigation of catalytic asymmetric reactions using the chiral ligands are in progress.

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