

Development of Manganese(III) Acetate along with Schiff-Base Ligands as the Catalyst for the Oxygenation of Olefins in the O₂/NaBH₄ System

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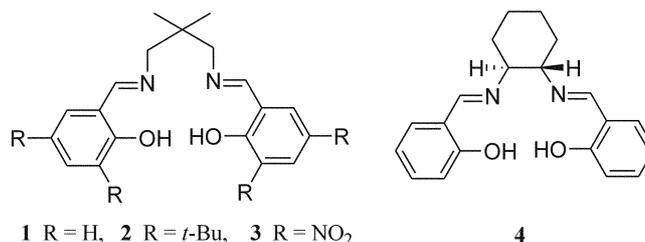
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Received May 17, 2004

Key Words : Molecular oxygen, Oxidation, Sodium borohydride, Manganese acetate, Schiff-base

As an oxidizing agent in organic synthesis, oxygen gas would be the most desirable oxidant in terms of costs and environmental considerations. Accordingly, development of efficient O₂-mediated oxidation methods has long been the research subject in chemistry.^{1,2} Previously, we have reported the oxidative conversion of olefins to the alcohols, where molecular oxygen was used as the oxidant. In this process, (schiff-base)Mn(III)Cl complexes were used as the catalyst, and sodium borohydride was employed as the required hydride source.^{3,4} As a continuing effort searching for the more practical oxygenation method, we have decided to examine a readily available manganese salt such as Mn(OAc)₃ or Mn(OAc)₂ as the catalyst.⁵

For the screening of the oxidation conditions, *trans*- β -methylstyrene was selected as the model compound. The olefin oxidation was performed using O₂ (1 atm), metal salt (8 mol%), schiff-base ligand (8 mol%) and NaBH₄ (2 equiv.) in the organic solvents (benzene and ethanol) at rt. The reaction was monitored using gas chromatography, and the product yields were obtained using dodecane as the internal standard. As the initial trial, the reaction was conducted in the absence of external ligands (entries 1-3). The salt of Mn(II) or Mn(III) species rarely provided the expected alcohol. Employment of one equivalent of Mn(III) salt also provided only 11% yield of the product (entry 2). However, addition of schiff-base type ligands led to great improvement in product yield. We have screened schiff-bases **1-4**, effective ligands in the (schiff-base)Mn(III) complexes employed previously.^{3,4} Among them, diaminopropane-derived ligand **1** showed the best result. For example, using **1**, the starting material was almost consumed (93% conversion) and the desired product was obtained in 91% yield (entry 4). The analogous ligands **2** and **3**, having electron rich and electron



poor properties compared to **1**, were selected for reactivity comparison. With these ligands, lower conversions of the olefin were observed (entries 5, 6). Trial of salen type ligand **4** also provided the lower reactivity (entry 7). These results suggested that choice of the ligand is critical to achieve the desired oxygenation. Examination of Mn(II) species as the catalyst, in the presence of ligand **1**, also afforded the good result giving the product in 85% yield (entry 8). This could be explained assuming that part of Mn(II)L is initially oxidized to Mn(III)L by O₂ under reaction conditions. Once Mn(III) species is developed, it could initiate oxidation system where Mn(III) and Mn(II) species are alternatively involved in the catalytic cycle. When other metal species such as Fe(III) or Co(II) were tried as the catalyst, the expected oxidation was not observed with lower conversion of the starting material (entries 9, 10).

In this process, (schiff-base)Mn(III) complexes formed *in situ* during the reaction is considered to be the active catalyst, otherwise the reactivity differences observed with ligand change could not be explained. In order to verify this assumption, the corresponding LMn(III)Cl (L = **1**, **2**, **4**) complexes were prepared, and the catalytic activity was compared (entries 4, 5, 7).⁶ In this reaction, the alcohol was obtained in respective 75%, 22%, and 60% yield, which is showing

Table 1. Examination of reaction conditions for the oxygenation of *trans*- β -methylstyrene

Ph-CH=CH-CH ₃ + O ₂ (1 atm) + NaBH ₄ (2 equiv.) + Catalyst (8 mol%) + Ligand (8 mol%)					benzene/ethanol		Ph-CH(OH)-CH ₂ -CH ₃		
					room temp. 4 hr				
Entry	Cat. ^a	Ligand	Conv. ^b (%)	Yield ^c (%)	Entry	Cat. ^a	Ligand	Conv. ^b (%)	Yield ^c (%)
1	Mn(III)	No	8	2	6	Mn(III)	3	61	49
2 ^d	Mn(III)	No	18	11	7	Mn(III)	4	42	24 (60) ^e
3	Mn(II)	No	7	1	8	Mn(II)	1	89	85
4	Mn(III)	1	93	91 (75) ^e	9	Fe(III)	1	23	0
5	Mn(III)	2	23	19 (22) ^e	10	Co(II)	1	38	3

^aMn(III) = Mn(OAc)₃·2H₂O; Mn(II) = Mn(OAc)₂·4H₂O; Fe(III) = FeCl₃; Co(II) = Co(OAc)₂·4H₂O. ^bConversion based on GC analysis using dodecane as an internal standard. ^cGC yields using dodecane as an internal standard. ^d100 mol% Mn(OAc)₃·2H₂O was employed. ^eYields obtained using the corresponding (schiff-base)Mn(III)Cl complex (8 mol%) as the catalyst.

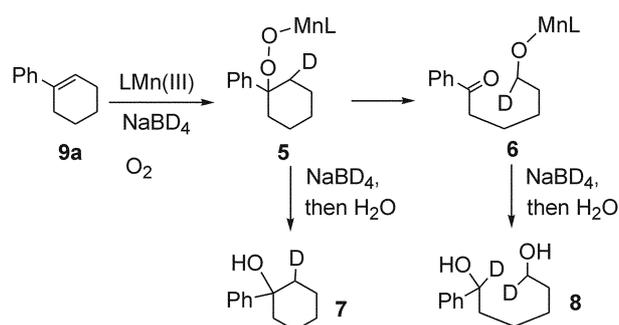
the similar reactivity trend. In addition, the complexation stabilities of the ligands **1-4** to the Mn(OAc)₃ could be partly responsible for the activity differences shown in Table 1.

Using the reaction condition of entry 4 in Table 1, various types of olefins were examined to achieve the desired oxidation. The results were summarized in Table 2.⁷ α -Methylstyrene was subjected to the reaction condition, the desired product was obtained in 78% yield (entry 2). In this case, non-oxidized dimeric product, 2,3-dimethyl-2,3-diphenylbutane, was isolated as the minor product. From our experience, dimeric product was obtained when substrate was too reactive under reaction condition. Thus, the less reactive ligand **4** was tried. As expected, the dimeric impurity was disappeared and the product **2b** was isolated in 90% yield (entry 2). When 1-phenylcyclohexene (**9a**) was used as the substrate, the expected alcohol **9b** and C-C cleaved product **9c** were isolated in 33% and 31% yield. Mechanistically, the products obtained from **9a** could be derived through the pathway described in Scheme 1.⁸ The suggested pathway was supported by the analysis of deuterium in the products obtained using NaBD₄. Involvement of LMn(III), NaBD₄, and O₂ produced the peroxomanganese intermediate **5**, which could be either reduced to **7** or fragmented to give the intermediate **6**. The ketone **6** could be further reduced to the diol **8** by NaBD₄.

Table 2. Oxidation of olefins using Mn(OAc)₃·2H₂O and schiff-base **1** as the catalyst

Olefins + O ₂ (1 atm) + 2.0 NaBH ₄		8 mol % Mn(OAc) ₃ ·2H ₂ O 8 mol % Ligand 1		Products	
		benzene/ethanol, rt, 4 hrs		Conv. ^a (%)	Yield ^b (%)
1			1b	100	58
2			2b	100	78 (90) ^c
3			3b	100	88
4			4b	100	71
5			5b	98	62 ^d
6			6b	100	64
7			7b	99	78
8			8b	99	76
9				97	9b + 9c (33)(31)

^aConversion was obtained based on GC analysis. ^bIsolated yields. ^cIsolated yield obtained when ligand **4** was employed instead of **1**. ^dAs a minor product, corresponding ketone was isolated in 15% yield.



Scheme 1

In this study, we have shown that readily available Mn salt, Mn(OAc)₃·2H₂O could be employed as the catalyst in the presence of appropriate schiff-base ligand. Atmospheric pressure of O₂ is used as the oxidant, and mild reducing agent NaBH₄ is used as the hydrogen source. The required ligand such as **1** is easily prepared from the condensation of diamine and salicyl aldehyde. This process affords the versatile reaction method, because different type of ligands can be employed to various olefinic substrates as needed. At present, further studies to extend the scope of this method as well as to identify the detailed reaction mechanism are underway.

Acknowledgment. This work was supported by grant No. R05-2004-000-10156-0 from the Korea Science & Engineering Foundation.

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- Examination of manganese(II) acetate with a nitrogen in the analogous olefin oxygenation has been reported to give low yield (< 40%). See, Hirao, T.; Mikami, S.; Ohshiro, Y. *Synlett.* **1990**, 541.
- Synthesis and isolation of the LMn(III)Cl (L = 3) complex could not be achieved.
- Typical reaction is as follows: In a 50 mL round bottomed flask were placed α -methylstyrene (**2a**, 1 mmol, 118 mg), ligand **1** (0.08 mmol, 26 mg), Mn(OAc)₃·2H₂O (0.08 mmol, 22 mg) and benzene/ethanol (10 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O₂. To this was added using syringe NaBH₄ (2 mmol, 78 mg) dissolved in 4 mL ethanol over 20 min, and the mixture was stirred for 4 hrs. After typical work-up, 2-phenyl-2-propanol (**2b**, 106 mg, 78% yield) was obtained as the product.
- For the mechanistic studies on analogous metalloporphyrin-catalyzed olefin oxygenation, see (a) Takeuchi, M.; Kano, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1726. (b) Takeuchi, M.; Koreda, M.; Kano, K.; Yoshida, Z.-I. *J. Mol. Catal.* **1996**, *113*, 51.