Mechanistic Studies on the O_2-mediated Oxidation of Olefins in the Presence of (Schiff-base)Mn(III) Catalyst and $NaBH_4$

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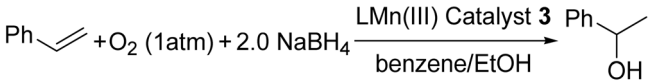
Received March 2, 2006

Key Words : Mechanism, Molecular oxygen, Oxygenation, (Schiff-base)Mn(III) complex, Sodium borohydride

Molecular oxygen would be the most desirable oxidant in organic synthesis due to its economically and environmentally favorable properties. A lot of efforts has long been made to utilize the oxygen molecule as the oxidizing reagent under mild reaction conditions. Probably, the most successful strategies have been the employment of the transition metals as the catalyst for the activation of oxygen molecule.

Recently, we have reported the oxidation of olefins to the corresponding alcohols using oxygen molecule as the oxidant, where (schiff-base)Mn(III) complexes were used as the catalysts in the presence of sodium borohydride (eq. 1).[1] During the study of this reaction, we were tempted to investigate reaction mechanism. Described here are the results of our experimental observations and subsequent mechanistic conclusions.



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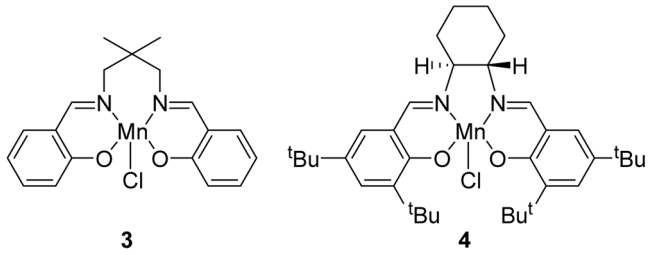
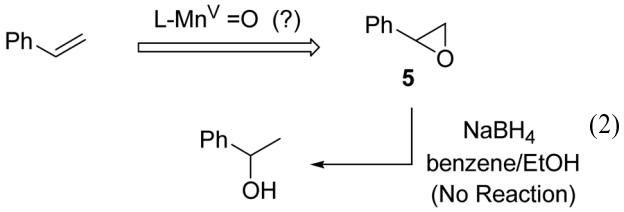


3 4

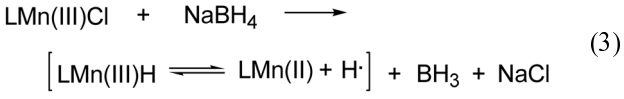
(Schiff-base)Mn(III) complexes have been utilized as the catalysts in the oxidation of some substrates such as olefins,[2] hydrocarbons,[3] and alcohols.[4] Mechanistically, asymmetric olefin epoxidation using (Salen)Mn(III) complex such as **4** has been well established. In these reactions, a high valent oxomanganese (^{V}Mn=O) species has been believed as an active oxidation component.[5]

First of all, we examined whether ^{V}Mn=O species were generated by O_2 in our condition using styrene as the substrate. Once oxo-manganese was developed during the reaction, it will convert styrene to styrene oxide (**5**). The epoxide **5** subsequently could be reduced to the alcohol by $NaBH_4$ under the reaction condition (eq. 2). However, no trace of the oxide **5** was observed when the reaction mixture was carefully examined by GC analysis. We also examined whether ring opening reaction of the epoxide **5** could occur in our system. When the authentic styrene oxide (**5**) was treated with $NaBH_4$ at room temperature, reduced alcohol was not observed at all. The starting material **5** was fully recovered intact. These results indicated that an oxomanganese(V) species is not involved in our oxidation process.



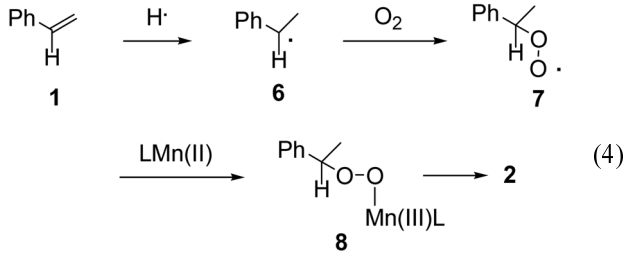
(2)

In the studies of metalloporphyrin-catalyzed oxygenation reactions, radical-mediated mechanism has been proposed.[6] We also conducted radical scavenging experiment. When the styrene oxidation was subjected to our condition in the presence of BHT (2,6-di^{t}butyl-4-methylphenol), oxidized product was not observed and all of the starting material was recovered. Thus, it is assumed that some radical species are involved as the reaction intermediates. Considering the reaction conditions in our system, it is reasonable to assume that hydrogen radical is working as the radical initiator. It is likely that hydride in $NaBH_4$ attack Mn(III)Cl to yield Mn(III)H species, which is homolytically cleaved to Mn(II) and hydrogen radical (H·) species (eq. 3).



(3)

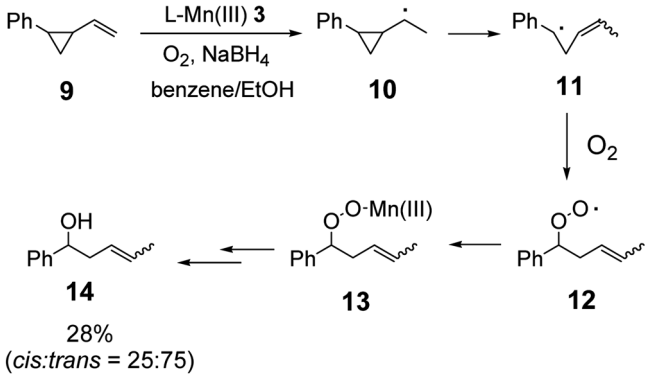
The generated hydrogen radical can add to C=C in styrene to give a benzylic radical **6**. Molecular oxygen can easily capture the radical **6** to produce peroxy radical **7**. The peroxy radical can react with Mn(II) to generate alkylperoxomanganese(III) species **8**, which can reduce to the benzylic alcohol **2** under the reaction condition (eq. 4).



(4)

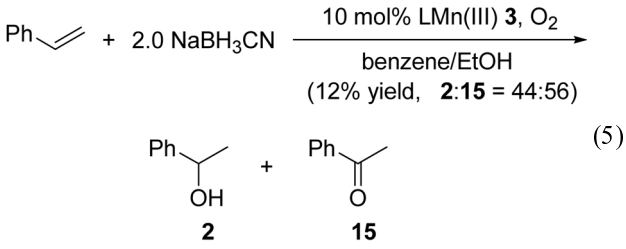
In this reaction, it is assumed that Mn(III) and Mn(II) species are involved in the catalytic cycle. The color change between colorless and dark brown was observed during the reaction, which indicated the involvement of colorless Mn(II) and dark brownish Mn(III) complexes.

In order to further confirm the generation of radical, 2-phenyl-1-vinylcyclopropane (**9**) was used as a radical clock substrate[7] in our system. When the olefin **9** was subjected to our reaction condition, the benzylic alcohol **14** was obtained as the major product (28% yield) along with some unidentified minor products. The product **14** was presumably obtained *via* a unsaturated peroxyl radical **12**, which is produced by the rapid ring opening of the cyclopropylmethyl radical **10** followed by reaction with O_2 (Scheme 1).



Scheme 1. Proposed mechanism for the oxygenation of vinylcyclopropane **9**.

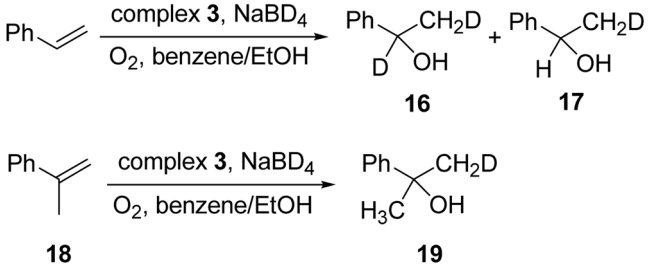
During the course of styrene oxidation, a small amount of acetophenone (< 5%) was detected by GC analysis. We were tempted to examine how acetophenone was derived. One possibility is that acetophenone was formed initially, and the subsequent reduction by $NaBH_4$ provided the alcohol **2** as the major product. We examined this possibility. The reaction was performed using $NaBH_3CN$ instead of $NaBH_4$ in order to capture the acetophenone as the intermediate, since the ketones are hardly reduced by $NaBH_3CN$. As an experimental result, the acetophenone (**15**) was obtained along with the corresponding alcohol in about one to one ratio (eq. 5). This result strongly implies that the alcohol and ketone are obtained *via* different synthetic pathways.



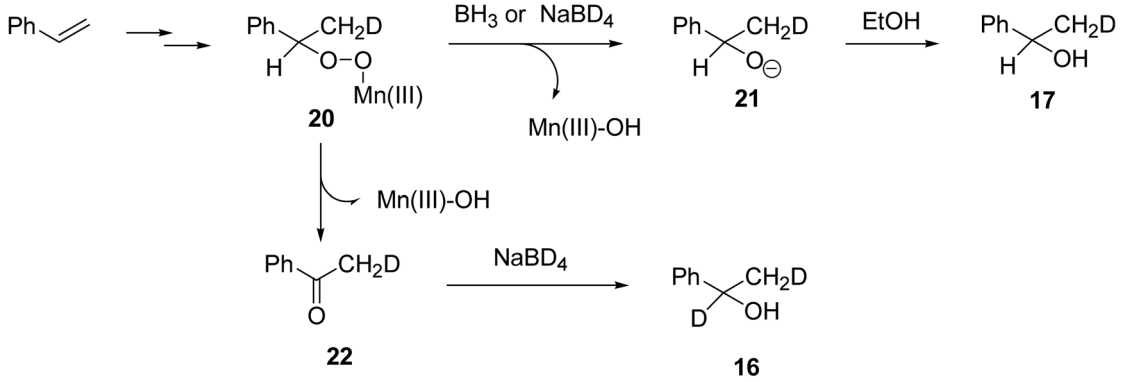
(5)

This observation could be explained by assuming that the cleavage of O-O bond in intermediate **8** (eq. 4) have two competing pathways. The one is unimolecular cleavage to form ketone **15** and the other is bimolecular reduction process to form corresponding alcohol **2** (see, Scheme 3).

In order to confirm this hypothesis, the deuterium incorporation experiment was studied using $NaBD_4$. The reaction conditions were the same as those described in experimental section, except for the use of $NaBD_4$ in place of $NaBH_4$. The structures of the oxygenation products of styrene and α-methylstyrene (**18**) were determined by ^1H NMR and GC-MS analysis (Scheme 2).



Scheme 2. Deuterium incorporation experiment using $NaBD_4$.



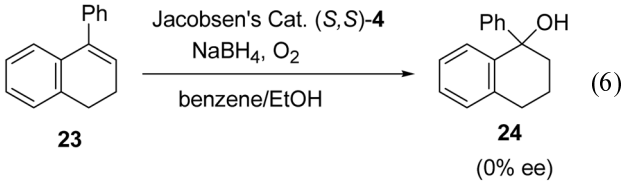
Scheme 3. Proposed competing reaction pathway from **20** to **21** and **22**.

In case of styrene, two molecular peaks were observed at *m/e* 123 and 124 (relative intensity; 1.6 : 1), corresponding to $C_6H_5CH(OH)CH_2D$ (**17**) and $C_6H_5CD(OH)CH_2D$ (**16**) respectively. The fragmentation peaks due to the $C_6H_5CH(OH)$ from **17** and $C_6H_5CD(OH)$ from **16** radical ions were also observed at *m/e* 107 and 108 (relative intensity: 1.6 : 1) respectively. The reaction products were also analyzed by means of ^{1}H NMR spectroscopy. The ^{1}H signal due to -CH(OH)- in **17** appeared at 4.85 ppm in a broad triplet (J = 6.6Hz) pattern, and the signal corresponding to -(CH_2D) in **17** appeared at 1.43 ppm (dt, J = 6.6 Hz, 1.7 Hz). While the ^{1}H signal for -(CH_2D) in **16** was not clearly shown due to overlapping at 1.41 ppm region, two ^{13}C NMR signals at 24.6 ppm and 24.8 as triplets (J = 19 Hz) confirm the presence of **16** in the mixture.

In the oxygenation of α-methylstyrene in the presence of $NaBD_4$, 1-deuterio-2-phenyl-2-propanol (**19**) was the sole oxygenation product, which was also confirmed by GC-MS and ^{1}H NMR analysis.

The experimental observation in Scheme 2 could be explained by suggestion of the pathway in Scheme 3. We can propose a common intermediate **20**, peroxo-Mn(III) species. The hydride in $NaBD_4$ or BH_3 can attack an electrophilic oxygen in -O-Mn(III) in **20** to form Mn(III)-OH and the leaving alkoxide **21**, which can be converted to **17**. As a competing process, the peroxy intermediate **20** can also be collapsed to ketone **22** and Mn(III)-OH in a unimolecular process. Subsequently, the resulting ketone **22** should be reduced to **16** by $NaBD_4$.

In the process of the formation of benzyl radical **6** and peroxy radical **7** in equation 4, it is possible to assume another pathway involving (alkyl)Mn(III) species. The (σ-alkyl)Mn(III) intermediate could be formed either by the coordination of olefin and Mn(III)-H complex or by the reaction between benzyl radical **6** (in eq. 4) and Mn(II) complex. If C-Mn(III) complex is made, it is reasonable to assume that chirality could be transferred when optically active (salen)Mn complex was employed as the catalyst. We examined this possibility using chiral Jacobsen's catalyst **4**. When 1-phenyl-3,4-dihydronaphthalene (**23**) was employed as the substrate, the optical yield of the alcohol **24** was never observed (eq. 6). Judging from this result, it is unlikely that coordination of (salen)Mn and benzylic carbon in the olefin is involved in this oxidation system.



(6)

From this study, we suggest that the oxidation is undergoing through alkylperoxo-Mn(III) species like **8** as the important intermediate. The intermediate **8** can either be cleaved to ketone or alcohol by the competing pathway. It is unlikely that the direct coordination between benzylic carbon in styrene and manganese complex is made in this pathway. Thinking about the overall radical process, this reaction is catalyzed by the alternative involvement of Mn(II) and Mn(III) complexes. Further investigation is still necessary to identify the more detailed reaction mechanism.

Experiment Section

Chemicals and instruments. Thin layer chromatography was performed on Merck prepared plates (silica gel 60 F-254 on aluminum). Column chromatography was performed using Merck silica gel 60 (230-400 mesh). NMR spectra were recorded on a JEOL (LAMBDA) NMR spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. GC/MSD analyses were carried out Hewlett-Packard 5772A gas chromatograph with a mass selective detector equipped with a HP-5 capillary column. The GC analyses were carried out on a YoungLin 600D instrument equipped with a FID detector using HP-5 capillary column. The optical yield (ee's) of the product was determined by GC equipped with a CYCLODEX B capillary column.

Typical experimental procedure of styrene oxidation. A typical example of the oxygenation of alkene is shown below. In a 50 mL round bottom flask were placed styrene (104 mg, 1.0 mmol), (Schiff-base)Mn(III) complex **3** (40 mg, 0.1 mmol) and benzene/EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O_2. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, the reaction was quenched by adding sat. NH_4Cl solution. Diethyl ether was added to the reaction mixture. The obtained organic layer was dried with Na_2SO_4, concentrated, and then purified by flash column chromatography to give 1-phenylethanol (99 mg, 81% yield) as the product. The structure was confirmed by analysis of NMR data; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (5H, m), 4.79 (1H, q, J = 6.4 Hz), 1.43 (3H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.0, 128.5, 127.5, 125.5, 70.3, 25.2.

Synthesis of *t*-2-phenyl-1-vinylcyclopropane (9). The compound **9** was synthesized in three steps. For the first step, *trans*-2-phenyl-1-cyclopropanecarboxylic acid (9.74 g, 0.06 mol) was treated with $LiAlH_4$ give to 2-phenylcyclopropanemethanol (7.99 g, 90% yield). In the second step, we carried out swern oxidation with 2-phenylcyclopropanemethanol (4.6 g, 31 mmol) to give 2-phenylcyclopropanecarbaldehyde (3.53 g, 78% yield). In the third step, Wittig reaction with 2-phenylcyclopropanecarbaldehyde (1.5 g, 10 mmol) was carried out to give the compound **9** (0.43 g, 30% yield). Through these reactions, the reaction conditions were not optimized. The structure of **9** was confirm by the analysis of NMR data; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (2H, m), 7.11 (1H, tt, J = 7.3 Hz, 1.2 Hz), 7.02 (2H, m), 5.49 (1H, dd, J = 17 Hz, 10.2 Hz, 8.5 Hz), 5.01 (1H, dd, J = 17 Hz, 1.5 Hz), 4.89 (1H, ddd, J = 10.2 Hz, 1.7 Hz), 1.88 (1H, m), 1.66 (1H, m), 1.16 (1H, ddd, J = 8.5 Hz, 5.6 Hz, 5.1 Hz), 1.06 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.3, 140.6,

128.3, 125.6, 125.5, 112.5, 27.5, 25.2, 16.7.

The oxygenation of *t*-2-phenyl-1-vinylcyclopropane (9). In a 50 mL round bottom flask were placed the compound **9** (144 mg, 1.0 mmol), (Schiff-base)Mn(III) complex **3** (40 mg, 0.1 mmol) and benzene/EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O_2. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, the reaction was quenched by adding sat. NH_4Cl solution. Diethyl ether was added to the reaction mixture. The obtained organic layer was dried with Na_2SO_4, concentrated, and then purified by flash column chromatography to give 1-phenyl-1-hydroxy-3-pentene (**14**, 46 mg, 28% yield) as the *cis/trans* isomer. The isomeric ratio was calculated by GC/Ms data. In addition, ^1H NMR analysis corresponding to methyl chemical shift at 1.68 ppm (for *trans* isomer) and 1.50 ppm (for *cis* isomer) also confirmed the isomeric ratio.

The asymmetric oxygenation of 1-phenyl-3,4-dihydronaphthalene (23). In a 25 mL flask were placed 1-phenyl-3,4-dihydronaphtalene (206 mg, 1 mmol), (*s,s*)-(+)-Jacobsen's catalyst **4** (32 mg, 0.05 mmol), and benzene/EtOH (2 mL/2 mL) as a solvent. After oxygen balloon was adapted to the reaction flask, the vessel was flushed three times by O_2. To this was added *via* syringe $NaBH_4$ (74 mg, 2 mmol) dissolved in 4 mL ethanol over 20 min with stirring. After the mixture was stirred for 4 hr at rt, the reaction was quenched by adding sat. NH_4Cl solution. Diethyl ether was added to the reaction mixture. The obtained organic layer was dried with Na_2SO_4, concentrated, and then purified by flash column chromatography to give 1-phenyl-1,2,3,4-tetrahydro-1-naphthalenol (**24**, 54 mg, 24% yield) as the product. The optical yield (ee's) of the product **24** was determined by GC equipped with CYCLODEX B capillary column. The structure was confirmed by NMR data analysis; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26 (9H, m), 2.96 (2H, m), 2.20 (2H, m), 2.07 (1H, m), 1.86 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.9, 141.9, 137.5, 128.9, 128.7, 127.6, 127.4, 126.5, 126.3, 75.3, 41.4, 29.8, 19.6.

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

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