(Nitrosonaphtholato)metal complex-catalyzed oxidation of phenols and alkenes

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Bis(1-nitroso-2-naphtholato)manganese(II), tris(1-nitroso-2-naphtholato)manganese(III), tris(2-nitroso-1-naphtholato)manganese(III), bis(1-nitroso-2-naphtholato)cobalt(II), bis(1-nitroso-2-naphtholato)nickel(II), bis(1-nitroso-2-naphtholato)copper(II) and bis(1-nitroso-2-naphtholato)zinc(II) were prepared and their catalytic abilities in the oxidation of phenols were examined. The best yields of diphenoquinones were obtained when the catalytic oxidation using bis(1-nitroso-2-naphtholato)manganese(II) was carried out at 23 °C under an oxygen atmosphere (1 atm) in the presence of a phosphine ligand. Likewise, phenols were completely converted to the corresponding diphenoquinones together with small amounts of benzoquinones under an oxygen pressure (20 atm) at 50 °C in a short period of time. It was proven that the manganese(II) catalyst, molecular oxygen, and phosphine ligand were essential for the catalytic phenol oxidation. On the other hand, bis(1-nitroso-2-naphtholato)manganese(II)-catalyzed epoxidation of alkenes was only effective when iodosylbenzene was used. The catalytic oxidation mechanism was discussed on the basis of the measurement of cyclic voltammograms of the (nitrosonaphtholato)metal complexes, isolated intermediates, and effect of additives.

Introduction

Discovery of catalysts which function efficiently under mild reaction conditions using molecular oxygen such as Gif type catalysts[1] is very important for the elucidation of the biological oxidation process, *e.g.*, P-450 electron-transfer oxidation in cells,[2] and the development of chemical industries like alkane oxidation under mild conditions.[3] In studies on the screening of non-metallo-porphyrin or -salen complexes as molecular oxygen carriers, we focused on (nitrosonaphtholato)metal complexes, [M(nnap)$_n$]. Many spectroscopic and physical investigations of [M(nnap)$_n$] complexes have been done over the course of the last three decades,[4] however, little is known about the catalytic ability of these complexes in organic reactions.[5] In an effort to further understand this system, we prepared some [M(nnap)$_n$] complexes and conducted the oxidation of 2,4- and 2,6-disubstituted phenols which were chosen due to their reactivity and structural simplicity.[6] It was thus shown that favorable results for the autoxidation of phenols were obtained using bis(1-nitroso-2-naphtholato)manganese(II), [Mn^{II}(1-nnap)$_2$]. We scrutinized the [Mn^{II}(1-nnap)$_2$]-catalyzed oxidation for the effect of additives, reaction temperatures, and oxygen pressures. As a result, it was discovered that the corresponding diphenoquinones were quantitatively obtained when the reactions were carried out in the presence of triphenylphosphine or tributylphosphine under oxygen (1 atm) at 23 °C. Increasing oxygen pressure (20 atm) led to complete conversion of phenols, but benzoquinones also formed under these conditions.

Epoxidation of alkenes is one of the most important reactions in organic synthesis because epoxides are versatile intermediates which can be converted to a variety of products.[3] In light of this fact, we extended the use of the [Mn^{II}(1-nnap)$_2$] complex to catalytic epoxidation of alkenes. Although this complex did not function as a molecular oxygen carrier in the epoxidation of aryl-substituted alkenes,[5] it showed a catalytic activity when iodosylbenzene was used as an oxidant. In this paper, we present a modified synthesis of [M(nnap)$_n$] complexes, catalytic oxidation of substituted phenols, catalytic epoxidation of alkenes, and discuss possible reaction mechanisms.

Results

Synthesis of (nitrosonaphtholato)metal complexes

Although it was reported that [Mn^{II}(1-nnap)$_2$] was prepared by addition of manganese(II) chloride to a diluted aqueous solution of 1-nitroso-2-naphthol,[4] we synthesized [Mn^{II}(1-nnap)$_2$] as a dark brown solid by treatment of manganese(II) chloride with sodium 1-nitroso-2-naphtholate, which was prepared by stirring 1-nitroso-2-naphthol in an aqueous sodium hydroxide solution (see Experimental section). A similar reaction of cobalt(II), nickel(II), copper(II) and zinc(II) chlorides with sodium 1-nitroso-2-naphtholate gave the corresponding bis(1-nitroso-2-naphtholato)metal(II) complexes. On the other hand, treatment of sodium 2-nitroso-1-naphtholate with manganese(II) chloride directly afforded tris(2-nitroso-1-naphtholato)manganese(III), [Mn^{III}(2-nnap)$_3$]. Tris(1-nitroso-2-naphtholato)manganese(III), [Mn^{III}(1-nnap)$_3$], was made by a ligand-exchange reaction of tris(pentane-2,4-dionato)manganese(III), [Mn(acac)$_3$], with 1-nitroso-2-naphthol in ethanol. All of the complexes were characterized by comparison with melting points and spectroscopic data in the literature,[4] measurement of cyclic voltammograms (Table 1), and elemental analyses. In addition, the structure of [Co^{II}(1-nnap)$_2$] was also confirmed by the magnetic susceptibility which showed μ_{eff} = 1.76 BM (295 K).[8]

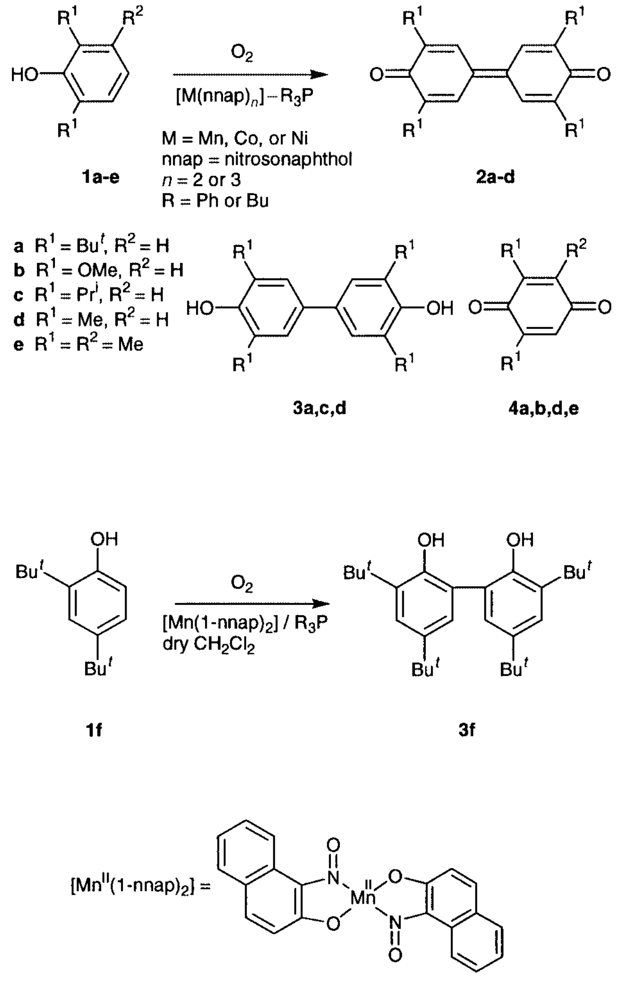
Catalytic oxidation of phenols

When a mixture of 2,6-di-*tert*-butylphenol (**1a**) and a catalytic amount of [Mn^{II}(1-nnap)$_2$] was stirred in dry dichloromethane at 23 °C under an oxygen atmosphere (1 atm), diphenoquinone **2a**† was formed in 5% yield after 10 h (Table 2, Entry 1 and Scheme 1). Addition of triphenylphosphine or tributylphosphine as a co-ligand[9] accelerated the oxidation to give the best results with yields of 93% attained (Table 2, Entries 3 and 4). The use of bidentate bis(diphenylphosphino)alkanes also gave **2a** in good yields along with a small amount of biphenyldiol **3a** (Table 2, Entries 5–8).

Triphenylphosphine oxide, pyridine and pyridine *N*-oxide[10] were not efficient as the co-ligand in this reaction (Table 2, Entries 9, 10). Although the catalytic activity of [Mn^{II}(1-nnap)$_2$] was also demonstrated in acetonitrile, tetrahydrofuran (THF), methanol and ethyl acetate (Table 2, Entries 11–14), no oxidation products were obtained in the reaction using benzene or acetic acid. The catalyst is insoluble in benzene and decomposes in acetic acid. Use of [Mn^{III}(1-nnap)$_3$] instead of [Mn^{II}(1-nnap)$_2$] also gave a good yield of **2a** (Table 3, Entry 1). Studies incorporating [Mn^{III}(2-nnap)$_3$] showed that it was not effective as a catalyst under the conditions (Table 3, Entry 2). When a similar reaction was carried out in the presence of [Co^{II}(1-nnap)$_2$] or [Ni^{II}(1-nnap)$_2$], more vigorous conditions were required in order to obtain **2a** (Table 3, Entries 3, 4). [Cu^{II}(1-nnap)$_2$] and [Zn^{II}(1-nnap)$_2$] complexes did not show any catalytic activity in the reaction (Table 3, Entries 5, 6).

In order to examine the oxygen pressure effect, [Mn^{II}(1-nnap)$_2$]-catalyzed oxidation of **1a** was conducted under 20, 40, 60 and 80 atm of oxygen, respectively. Under these conditions, **1a** was completely consumed after 6 h, although a significant pressure effect did not appear. On the contrary, the high pressure conditions led to the formation of **4a** (Table 4, Entry 2). The best yield of **2a** was obtained at 50 °C under 20 atm of oxygen (Table 4, Entry 5). Interestingly, use of two equivalents of triphenylphosphine under 20 atm of oxygen preferentially yielded **4a** (Table 4, Entry 4).

The catalytic oxidation was applied to other substituted phenols **1b**–**f**, and the catalytic ability of the [Mn^{II}(1-nnap)$_2$] complex was confirmed (Table 4, Entries 6–13). The results are shown in Table 4.



Scheme 1

Table 1 Redox potentials of (nitrosonaphtholato)metal complexes in dichloromethane containing 0.1 M tetrabutylammonium perchlorate at $v = 50$ mV s^{-1}[a]

[M(1-nnap)$_n$]	E_{pc}/V	E_{pa}/V	ΔE_p/mV	$E'_{1/2}$/V	$E_{1/2}$/V[b]
[Mn^{II}(1-nnap)$_2$]	−0.500	−0.379	121	−0.440	−0.435
[Mn^{III}(1-nnap)$_3$]	−0.483	−0.398	85	−0.441	−0.436
[Mn^{III}(salen)]Cl[c]	−0.701	−0.595	106	−0.648	−0.651
[Co^{II}(1-nnap)$_2$]	−1.161	−1.056	105	−1.109	−1.116
[Ni^{II}(1-nnap)$_2$]	0.417	0.482	65	0.450	0.452
[Zn^{II}(1-nnap)$_2$]	—	0.755	—	—	0.702

[a] All potentials were corrected by the use of E_{Fc/Fc^+}. [b] $E_{1/2}$ was determined by differential pulse polarography. [c] To compare the redox potentials, the complex was measured (salen = bis(salicylidene)ethylenediaminato).

Table 2 [Mn(1-nnap)$_2$]-catalyzed oxidation of 2,6-di-*tert*-butylphenol (**1a**) at 23 °C[a]

Entry	Molar ratio[b]	Additive	Solvent	Time/h	Product (Yield (%))[c] 2a	3a	Recovery (%)[d]
1	1:0.1:0	none	CH_2Cl_2	10	5		86
2	1:0.1:0.6	Ph_3P	CH_2Cl_2	10	52		32
3	1:0.1:1.1	Ph_3P	CH_2Cl_2	20	93		0
4	1:0.1:1.1	Bu_3P	CH_2Cl_2	5	93		0
5	1:0.1:1.1	$Ph_2PCH_2PPh_2$	CH_2Cl_2	5	53	4	36
6	1:0.1:1.1	$Ph_2P(CH_2)_2PPh_2$	CH_2Cl_2	5	71	23	0
7	1:0.1:1.1	$Ph_2P(CH_2)_3PPh_2$	CH_2Cl_2	5	71	16	trace
8	1:0.1:1.1	$Ph_2P(CH_2)_4PPh_2$	CH_2Cl_2	5	76		trace
9	1:0.1:1.1	Ph_3PO	CH_2Cl_2	10	27		70
10	1:0.1:1.1	Py	CH_2Cl_2	10	10		84
11	1:0.1:1.1	Ph_3P	CH_3CN	10	86		trace
12	1:0.1:1.1	Ph_3P	THF	10	80	10	trace
13	1:0.1:1.1	Ph_3P	CH_3OH	10	73		12
14	1:0.1:1.1	Ph_3P	AcOEt	10		79	14

[a] The reaction mixture was stirred under an oxygen atmosphere (1 atm). [b] **1a**:[Mn(1-nnap)$_2$]:additive. [c] Isolated yield based on the amount of **1a** used. [d] **1a** recovered after work up.

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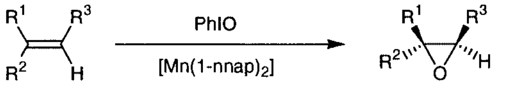
† Diphenoquinone is [bicyclohexa-2,5-dien-1-ylidene]-4,4′-dione.

Catalytic epoxidation of alkenes

Since it has become apparent that the manganese, cobalt and nickel complexes exhibit catalytic activities in the phenol oxidation, we applied the (nitrosonaphtholato)metal complexes to catalytic epoxidation of aryl-substituted alkenes. Epoxidation of *trans*-stilbene (**5a**), however, did not proceed under an oxygen atmosphere.[5] None of hydrogen peroxide, *tert*-butylhydroperoxide and sodium hypochlorite was effective as oxidant. When the reaction of **5a** with iodosylbenzene in the presence of [Mn^{II}(1-nnap)$_2$] was carried out in dichloromethane at 23 °C under argon, only 6% of the corresponding epoxide **6a** was obtained (Scheme 2). A similar reaction in acetonitrile at 50 °C improved the yield of **6a** (Table 5, Entry 1).



5a-d   **6a-d**

a R^1 = H, R^2 = R^3 = Ph
b R^1 = R^3 = Ph, R^2 = H
c R^1 = Ph, R^2 = R^3 = H
d R^1 = R^2 = R^3 = Ph

Scheme 2

A blank experiment without [Mn^{II}(1-nnap)$_2$] was carried out, however, the corresponding epoxide was not obtained. It was reported that addition of pyridine *N*-oxide increased the yield of epoxides in the [Cr^{III}(salen)]$^+$ catalytic system,[10] however, pyridine *N*-oxide, triphenylphosphine oxide and pyridine did not influence the [Mn^{II}(1-nnap)$_2$]-catalyzed epoxidation. *cis*-Stilbene (**5b**) gave a mixture of *trans*-stilbene oxide (**6a**) and *cis*-stilbene oxide (**6b**) (Table 5, Entry 2). Styrene (**5c**) and 1,1,2-triphenylethene (**5d**) also afforded the corresponding epoxides (**6c**,**d**) (Table 5, Entries 3 and 4). Use of [Mn^{III}(1-nnap)$_3$], [Co^{II}(1-nnap)$_2$] and [Ni^{II}(1-nnap)$_2$] led to similar results (Table 5, Entries 5–7).

Discussion

The measurements from the cyclic voltammogram of [Mn^{II}-(1-nnap)$_2$] showed reversible Mn(II)$\rightleftharpoons$Mn(III) and irreversible Mn(III)$\rightarrow$Mn(IV) processes. This indicates that [Mn^{II}(1-nnap)$_2$] tends to be oxidized to Mn(III) species. In other words, it could work as a one-electron transfer catalyst. In fact, the presence of 0.1 equivalent of [Mn^{II}(1-nnap)$_2$] led to a 5% yield of **2a** (Table 2, Entry 1). Since phosphine compounds are known to activate some metal catalysts,[3,9,10] the activation of [Mn^{II}(1-nnap)$_2$] was examined by use of phosphine ligands. Addition of triphenylphosphine or tributylphosphine to the [Mn^{II}(1-nnap)$_2$] complex brought about the quantitative conversion of **1a** to **2a** at room temperature and the phosphine co-ligands added were also transformed into the corresponding oxides, quantitatively (Table 2, Entries 3 and 4). When a similar reaction was carried out in the absence of the catalyst or under an argon atmosphere, the oxidation did not progress at all. In addition, only the use of triphenylphosphine in the absence of **1a** at the molar ratio of [Mn^{II}(1-nnap)$_2$] : PPh$_3$ = 0.1 : 1 in dichloromethane at 23 °C for 20 h under an oxygen atmosphere resulted in the production of triphenylphosphine oxide in 41% yield after the TLC separation. On the basis of these results, it could be assumed

Table 3 Catalytic oxidation of 2,6-di-*tert*-butylphenol (**1a**) in the presence of various (nitrosonaphtholato)metal complexes[a]

Entry	[M(nnap)$_n$]	Solvent	Temp./°C	Product (Yield (%))[b] 2a	4a	Recovery (%)[c]
1	[Mn^{III}(1-nnap)$_3$]	CH$_2$Cl$_2$	23	88		trace
2	[Mn^{III}(2-nnap)$_3$]	CH$_2$Cl$_2$	23	39	2	54
3	[Co^{II}(1-nnap)$_2$]	CH$_3$CN	50	29	14	45
4	[Ni^{II}(1-nnap)$_2$]	CH$_3$CN	reflux	44		43
5	[Cu^{II}(1-nnap)$_2$]	CH$_2$Cl$_2$	23			83
6	[Zn^{II}(1-nnap)$_2$]	CH$_3$CN	23			90

[a] The reaction mixture was stirred under an oxygen atmosphere (1 atm) for 10 h at the molar ratio of **1a** : [M(nnap)$_n$] : Ph$_3$P = 1 : 0.1 : 1.1. [b] Isolated yield based on the amount of **1a** used. [c] **1a** recovered after work up.

Table 5 (Nitrosonaphtholato)metal-catalyzed epoxidation of alkenes with iodosylbenzene[a]

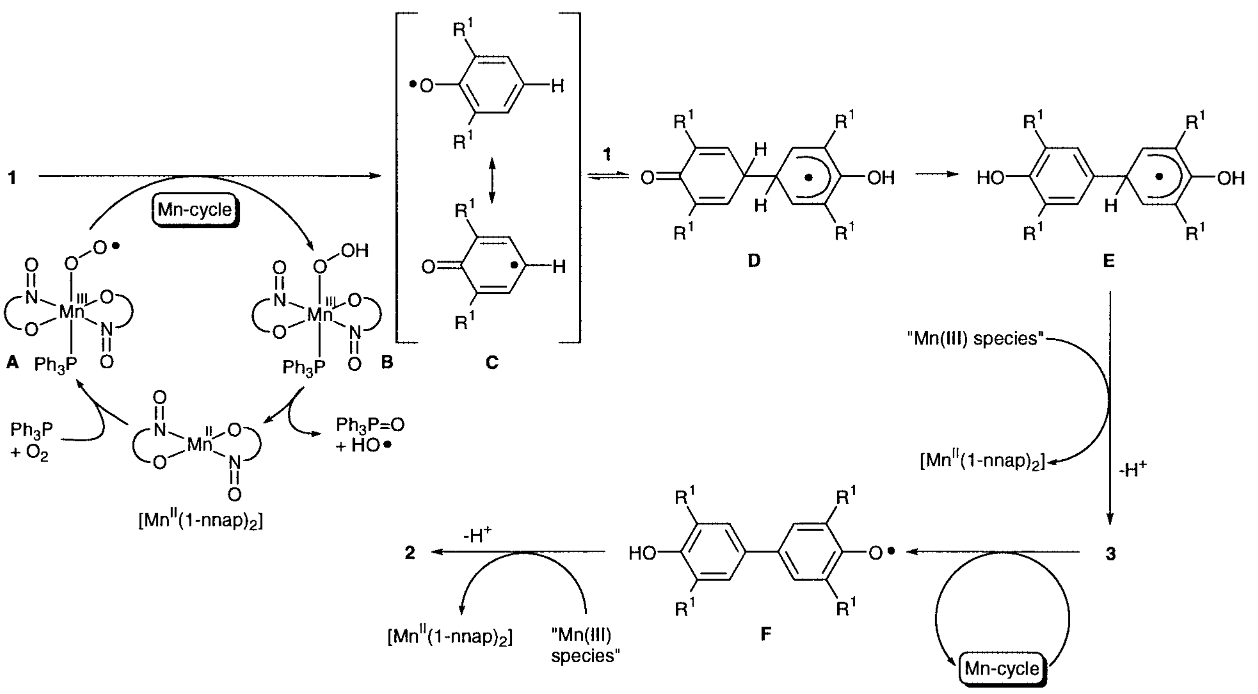
Entry	Substrate	Catalyst	Temp./°C	Product (Yield (%))[b]	
1	**5a**	[Mn(1-nnap)$_2$]	50	**6a** (26)	
2	**5b**	[Mn(1-nnap)$_2$]	23	**6a** (18)	**6b** (14)
3	**5c**	[Mn(1-nnap)$_2$]	23	**6c** (28)	
4	**5d**	[Mn(1-nnap)$_2$]	23	**6d** (21)	
5	**5a**	[Mn(1-nnap)$_3$]	50	**6a** (25)	
6	**5a**	[Co(1-nnap)$_2$]	50	**6a** (22)	
7	**5a**	[Ni(1-nnap)$_2$]	50	**6a** (14)	

[a] The reaction was carried out at the molar ratio of alkene–catalyst–iodosylbenzene = 1 : 0.1 : 5 in acetonitrile under an argon atmosphere for 10 h. [b] Isolated yield based on the amount of the alkene used.

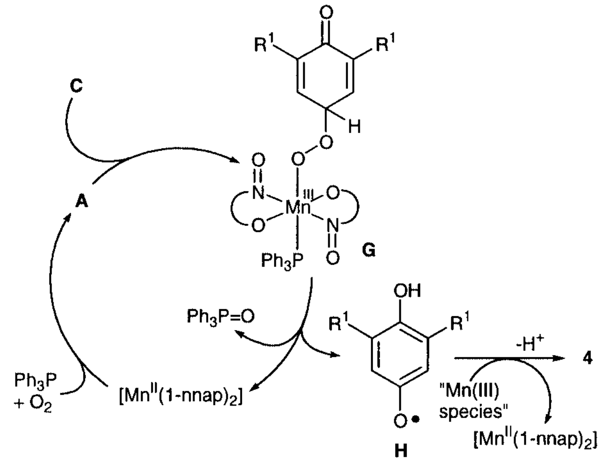
Table 4 [Mn(1-nnap)$_2$]-catalyzed oxidation of substituted phenols **1a**–**f**[a]

Entry	Phenol	Molar ratio[b]	Pressure/atm	Temp./°C	Time/h	Product (Yield (%))[c]		Recovery (%)
1	**1a**	1 : 0.1 : 1.1	1	23	20	**2a** (93)		0
2	**1a**	1 : 0.1 : 1.1	20	23	6	**2a** (67)	**4a** (29)	0
3	**1a**	1 : 0 : 1.1	20	23	6	**2a** (0)	**4a** (0)	90
4	**1a**	1 : 0.1 : 2.2	20	23	6	**2a** (4)	**4a** (77)	0
5	**1a**	1 : 0.1 : 1.1	20	50	3	**2a** (77)	**4a** (22)	0
6	**1b**	1 : 0.1 : 1.1	1	23	10	**2b** (75)		16
7	**1b**	1 : 0.1 : 1.1	20	50	3	**2b** (76)	**4b** (23)	0
8	**1c**	1 : 0.1 : 1.1	1	23	10	**2c** (56)		39
9	**1c**	1 : 0.1 : 1.1	20	50	3	**2c** (74)		trace
10	**1d**	1 : 0.1 : 1.1	20	50	3	**2d** (26)	**3d** (10) **4d** (26)	8
11	**1e**	1 : 0.1 : 1.1	20	50	3		**4e** (15)	trace[e]
12	**1f**[d]	1 : 0.1 : 1.1	1	23	10		**3f** (47)	47
13	**1f**	1 : 0.1 : 1.1	20	50	3		**3f** (72)	trace[e]

[a] The reaction was performed in the presence of triphenylphosphine. [b] **1** : [Mn(1-nnap)$_2$] : PPh$_3$. [c] Isolated yield based on the amount of phenol used. [d] Tributylphosphine was used instead of triphenylphosphine. [e] A complex mixture was formed.



Scheme 3



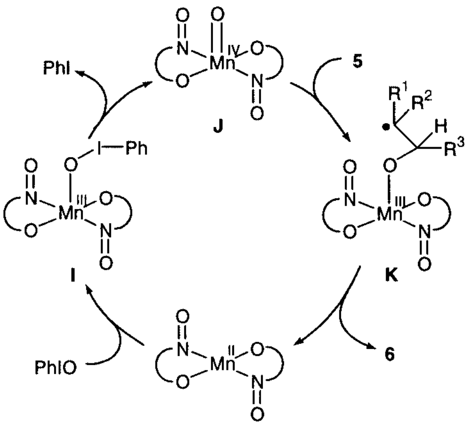
Scheme 4

that [Mn^{II}(1-nnap)$_2$] catalyst was activated by the phosphine ligand and molecular oxygen was trapped to form a new complex **A** at the first stage (Scheme 3).

The oxidation state of **A** should be Mn(III) since the Mn(III) species is electrochemically stable. Although the exact reasoning is not known, the phosphine ligand probably plays an important role in the stability of **A**. We tried to observe the change for the electronic spectrum of **A** but, unfortunately, a significant change was not seen because of the presence of a strong band based on a $\pi\rightarrow\pi^*$ transition at 414 nm of [Mn^{II}(1-nnap)$_2$]. The phenoxy hydrogen of **1** must be abstracted by the active complex **A** to give peroxymanganese(III) complex **B** and phenoxyl radical **C**. The peroxymanganese(III) complex **B** would immediately decompose under the reaction conditions to yield phosphine oxide and hydroxyl radical which is transformed to oxygen and water.[3a,11] At this stage, the [Mn^{II}(1-nnap)$_2$] catalyst could be regenerated and one catalytic cycle would be constructed. On the other hand, the phenoxyl radical **C** should react with **1** to give **D** which isomerizes to **E**. The radical **E** should take part in a similar oxidation cycle, and diphenyldiol **3** would be formed. The diphenyldiol **3** is oxidized by the same catalytic cycle in dichloromethane, acetonitrile, THF and methanol to yield **F**, which is transformed to the final product **2** *via* a similar oxidation system again (Table 2, Entries 2–8, 11–13). The plausible mechanism is also supported by the isolation of **3** which was oxidized under the same reaction conditions to quantitatively give **2**,[6a] and the fact that the added phosphine ligand converted to the corresponding phosphine oxide. However, the stoichiometry in molecular oxygen and the phosphine ligand is not clear at this moment.

It was observed that increasing oxygen pressure caused the formation of benzoquinone **4** to some extent (Table 4, Entries 2, 4, 7, 10, 11). It was thought that raising the oxygen pressure led to the increased probability of formation of **A**, which resulted in the acceleration of the reaction of **A** with **C** (Scheme 4). This interaction releases phenoxyl radical **H** and triphenylphosphine oxide, reproducing [Mn^{II}(1-nnap)$_2$] by a subsequent one-electron transfer in intermediate complex **G**. The phenoxyl radical **H** should be oxidized by a similar catalytic cycle mentioned in Scheme 3 to produce benzoquinone **4**. It might be considered that direct oxidation of **H** with molecular oxygen with increasing oxygen pressure would also occur. However, it is apparent that the Mn^{II} catalyst plays an important role in the reaction since the reaction did not proceed in the absence of the Mn^{II} catalyst (Table 4, Entry 3).

There are many reports suggesting that higher valent oxo-manganese species participate in most catalytic epoxidations.[3c,12] [Mn^{II}(1-nnap)$_2$] would be somewhat oxidized by iodosylbenzene to afford **I** and then **J** which is the most plausible oxygen carrier intermediate in this reaction (Scheme 5).



Scheme 5

The complex **J** will react with alkene **5** according to the mechanism proposed in the literature[12] to form epoxide **6** and regenerate [Mn^{II}(1-nnap)$_2$]. Racemization of the epoxide in the reaction using *cis*-stilbene (**5b**) (Table 5, Entry 2) supports the fact that a radical intermediate such as **K** must be involved in the catalytic cycle,[12] however, it seemed that [Mn^{II}(1-nnap)$_2$] complex was only allowed to exist in the Mn(II)$\rightleftharpoons$Mn(III) state, while the Mn(III)$\rightleftharpoons$Mn(IV) redox state or a higher-valent state was forbidden because of accompanying decomposition of the complex based on the result of electrochemical measurement. Therefore, the complex **J** would decompose to some extent before oxygen transfer to **5**. That is, this catalytic epoxidation was not efficient in contrast to the results reported.[5] It is possible that the oxidant, such as molecular oxygen, *tert*-butylhydroperoxide and sodium hypochlorite, was too weak to produce a high-valent complex like **J**, which explains why the attempted epoxidation using these oxidants failed. In addition, it seems that peroxyl radical complex **A** as shown in Scheme 3 is unique in its ability to abstract hydrogen from the hydroxy group since a co-ligand such as triphenylphosphine was not effective in this epoxidation. Use of [Mn^{III}(1-nnap)$_3$] also led to a similar result of [Mn^{II}(1-nnap)$_2$]-catalyzed epoxidation (Table 5, Entry 5). It might be due to the instability of the corresponding high-valent oxo-manganese species since [Mn^{III}(1-nnap)$_3$] also resisted electrochemical oxidation to Mn(IV).

Conclusion

[Mn^{II}(1-nnap)$_2$] was the most effective catalyst in the oxidation of phenols **1** under an oxygen atmosphere. Phosphine compounds were essential as co-ligands for the oxidative conversion of **1** to diphenoquinones **2**. During the oxidation, it seemed that at least four catalytic cycles as shown in Scheme 3 participated in the formation of diphenoquinone **2**. Raising the oxygen pressure led to the production of benzoquinone **4** since the reaction of peroxymanganese complex **A** with phenoxyl radical **C** was accelerated under these conditions. Although (nitrosonaphtholato)metal complex-catalyzed epoxidation of aryl-substituted alkene **5** was not efficient, formation of the corresponding epoxides **6** was possible using iodosylbenzene.

Experimental

Measurements

All of the ^{1}H NMR spectra were recorded by a JNM PMX-60SI (60 MHz) spectrometer with TMS being used as the internal standard. The chemical shifts are shown as δ values (ppm). The IR spectra were measured on a JASCO A-102 IR spectrometer. The IR spectral data are expressed in cm^{-1}. Mass spectra were recorded by a JNM DX-300 mass spectrometer. The UV–visible spectra were taken by a Hitachi U-4000 spectrophotometer in CH_2Cl_2. The electrochemical measurements of the (nitrosonaphtholato)metals were carried out on a Yanagimoto Polarographic Analyzer P-1100 in CH_2Cl_2 equipped with three electrodes, using a glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference. Tetrabutylammonium perchlorate (*ca.* 1×10^{-1} mol dm^{-3}) was employed as the supporting electrolyte. Magnetic susceptibility of [Co^{II}(1-nnap)$_2$] was measured on a Faraday balance. The apparatus was calibrated with [Ni(en)$_3$][S_2O_3] (en = ethane-1,2-diamine).[13] Diamagnetic corrections were made by Pascal's constant.[14] The effective magnetic moment was calculated using the equation $\mu_{eff} = 2.828 (\chi^{AT})^{1/2}$, where χ^A is the magnetic susceptibility per cobalt atom. The GC was recorded by a HP-6590 apparatus equipped with a fused-silica capillary column. The HPLC was performed by a Hitachi HPLC apparatus equipped with an RP-18 ODS packed column eluting with MeOH. All of the melting points were determined by a Yanaco micromelting-point apparatus MP-J3 and were uncorrected. The reactions under high pressure were carried out in a glass tube using a Taiastu Glass stainless steel reactor.

Materials

2-Naphthol, 1-naphthol, 2,6-di-*tert*-butylphenol (**1a**), 2,6-dimethoxyphenol (**1b**), 2,6-diisopropylphenol (**1c**), 2,4-dimethylphenol (**1e**), *trans*-stilbene (**5a**), styrene (**5c**), $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, triphenylphosphine, tributylphosphine, pyridine (Wako), bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane (Kanto) and 2,6-dimethylphenol (**1d**), *cis*-stilbene (**5b**), pyridine *N*-oxide, iodobenzene diacetate (Aldrich) were used as received. [Mn(acac)$_3$],[15] 1,1,2-triphenylethene[16] and iodosylbenzene[17] were prepared according to the methods described in the literature. Solvents were reagent grade and in many cases were dried before use.

Preparation of 1-nitroso-2-naphthol

After 2-naphthol (29 g) was dissolved in hot 0.6 M NaOH (340 cm^3), the solution was cooled to 0 °C. $NaNO_2$ (14 g) was added, and 6 M H_2SO_4 (31 cm^3) was carefully dropped into the solution during 1.5 h with stirring. The mixture was stirred for 1 h. The brown solid which formed was filtered, washed with water, and dried in a desiccator. The crude material was recrystallized from ligroin (bp 75–120 °C) to give 1-nitroso-2-naphthol (14 g, 40%) as reddish-brown needles, mp 107–109 °C (lit.,[18] mp 106–108 °C).

Preparation of 2-nitroso-1-naphthol

To a heated solution of 95% EtOH in which fused $ZnCl_2$ (5.0 g) and 1-naphthol (3.3 g) were dissolved, $NaNO_2$ (2.5 g) was slowly added. The mixture was heated under reflux for 3 h. The solid which formed was filtered, washed with EtOH, and dried. The solid was dissolved in water, which was acidified with conc. HCl. A brown solid was formed again, filtered, and recrystallized from EtOH to give 2-nitroso-1-naphthol as reddish-brown microcrystals (3.26 g, 36%), mp 154.2–156.1 °C (decomp.) (lit.,[18] mp 156 °C (decomp.)).

Preparation of nitrosonaphthol sodium salt

1-Nitroso-2-naphthol (2.0 g) was dissolved in a 10 M NaOH solution (50 cm^3) at 0 °C during 2 h, and the mixture was stirred at room temperature overnight. A green solid which formed was filtered, washed with 2 M NaOH solution, and dried in a desiccator to give the corresponding sodium salt (2.0 g, 90%). 2-Nitroso-1-naphthol sodium salt was also prepared in a similar manner to that described above.

Preparation of [Mn^{II}(1-nnap)$_2$]

Sodium 1-nitroso-2-naphtholate (2.7 g) was dissolved in water (200 cm^3), and $MnCl_2$ (1.6 g) was added. After stirring for 2 h, the solid which had formed was filtered, thoroughly washed with water, and dried in a desiccator. The solid was recrystallized from CH_2Cl_2–hexane to give dark-brown crystals (1.45 g, 46%) (Found: C, 59.96; H, 3.13; N, 6.83%. Calcd. for $C_{20}H_{12}O_4N_2Mn$: C, 60.17; H, 3.02; N, 7.02%), mp over 300 °C; ν_{max}($CHCl_3$)/cm^{-1} 1510 (N=O); λ_{max}(CH_2Cl_2)/nm 414 (log ε 4.33).

Preparation of [Mn^{III}(1-nnap)$_3$]

After [Mn(acac)$_3$] (0.34 g) was dissolved in EtOH (100 cm^3), 1-nitroso-2-naphthol (1.29 g) was added, and the mixture was stirred for 5 h at room temperature. Hexane (100 cm^3) was added to initiate crystal growth. The solid obtained was recrystallized from CH_2Cl_2–hexane: 0.65 g (50%) (Found: C, 62.92; H, 3.18; N, 7.12%. Calcd. for $C_{30}H_{18}O_6N_3Mn$: C, 63.06; H, 3.18; N, 7.35%); dark-brown microcrystals, mp over 300 °C; ν_{max}(KBr)/cm^{-1} 1505 (N=O); λ_{max}(CH_2Cl_2)/nm 421 (log ε 4.51).

Preparation of other [M^{II}(1-nnap)$_2$] complexes

Other [M^{II}(1-nnap)$_2$] complexes were synthesized by the reaction of sodium 1-nitroso-2-naphtholate with the corresponding metal(II) chlorides by a method similar to that described above. The IR spectra of these complexes were identical with those found in literature.[4a]

[Co^{II}(1-nnap)$_2$]. Red microcrystals, mp 275 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1516 (N=O); λ_{max}(CH_2Cl_2)/nm 407 (log ε 4.30).

[Ni^{II}(1-nnap)$_2$]. Brown microcrystals, mp 93 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1552 (N=O); λ_{max}(CH_2Cl_2)/nm 411 (log ε 3.95).

[Cu^{II}(1-nnap)$_2$]. Brown microcrystals, mp over 300 °C; ν_{max} (KBr)/cm^{-1} 1524 (N=O); λ_{max}(CH_2Cl_2)/nm 417 (log ε 4.32).

[Zn^{II}(1-nnap)$_2$]. Green microcrystals, mp over 300 °C; ν_{max} (KBr)/cm^{-1} 1554 (N=O); λ_{max}(CH_2Cl_2)/nm 393 (log ε 4.18).

[Mn^{III}(2-nnap)$_3$]. (Found: C, 63.60; H, 3.17; N, 6.84%. Calcd. for $C_{30}H_{18}O_6N_3Mn$: C, 63.06; H, 3.18; N, 7.35%); dark brown microcrystals, mp over 300 °C; ν_{max} ($CHCl_3$)/cm^{-1} 1508 (N=O).

Catalytic oxidation of phenols 1a–f

A mixture of phenol **1** (1 mmol), (nitrosonaphtholato)metal complex (0.1 mmol) and phosphine ligand (1.1 mmol) was stirred in dry CH_2Cl_2 (30 cm^3) at 23 °C under an oxygen atmosphere (normally 1 atm). After quenching with 2 M HCl, the aqueous mixture was extracted with CH_2Cl_2. The extract was concentrated to dryness, and the products were separated by silica gel TLC (Wakogel B-10) with $CHCl_3$ or Et_2O–hexane (1 : 9 v/v) as the developing solvents. Melting points, R_f values, retention times, IR and ^{1}H NMR spectra of diphenoquinones **2a**–**d**, diphenyldiols **3a**,**c**,**d**,**f** and benzoquinones **4a**,**b**,**d**,**e** were identical with those of the authentic samples.[6,19,20]

Catalytic epoxidation of alkenes 5a–d

A mixture of alkene **5** (1 mmol), iodosylbenzene (1–5 mmol) and (nitrosonaphtholato)metal complex (0.1 mmol) was stirred in dry MeCN (30 cm^3) for 10 h under an argon atmosphere. After quenching with saturated $NaHSO_3$ (2 cm^3) and saturated $NaHCO_3$ aqueous solution (30 cm^3), the mixture was extracted with CH_2Cl_2. The extract was concentrated to dryness and the residue was separated by silica gel TLC using CH_2Cl_2–hexane (1 : 1 v/v) as the developing solvents. Melting points, R_f values, retention times, IR and ^{1}H NMR spectra of epoxides **6a**–**d** were identical with those of the authentic samples.[21]

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