THE HIGHLY EFFICIENT OXIDATION OF OLEFINS, ALCOHOLS, SULFIDES AND ALKANES WITH HETEROAROMATIC *N*-OXIDES CATALYZED BY RUTHENIUM PORPHYRINS

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Abstract–The oxygen atom transfer reactions from 2,6-disubstituted pyridine *N*-oxides to olefins, allyl or benzyl alcohols and sulfides were efficiently catalyzed by ruthenium porphyrins, and these substrates were converted into epoxides, aldehydes and sulfoxides, respectively, with high selectivity These oxidations also proceeded using other heteroaromatic *N*-oxides, such as pyrazine *N*-oxides, as oxidants. The catalytic activity of ruthenium porphyrin complexes was enhanced by the addition of a small amount of HCl or HBr In the presence of these acids, the oxidations of alkanes or aliphatic alcohols with 2,6-dichloropyridine *N*-oxides were also efficiently catalyzed by ruthenium porphyrin complexes, and alcohols or ketones were afforded as oxidation products with high selectivity In the hydroxylation of adamantane, ruthenium porphyrins work very efficiently as catalysts, giving a turnover number of up to 120000. This system offers practical advantages, such as mild conditions, tractability of oxidants and easy overall procedures. In the case of the reactions with HCl or HBr, one possibility in the reaction mechanism is that the activity of ruthenium porphyrins is enhanced in part by the coordination of Cl^- or Br^- as axial ligands.

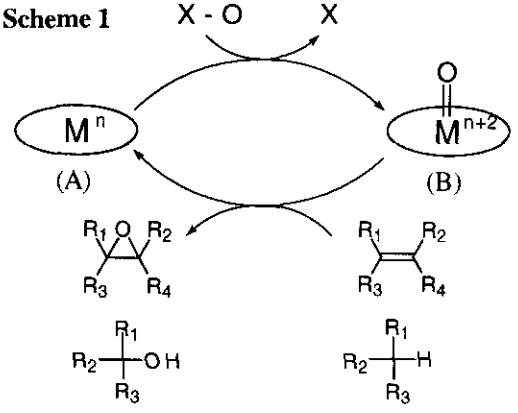
INTRODUCTION

Much progress has been made in the oxidation of saturated hydrocarbons or other unreactive compounds with transition metal catalysts, but it remains a challenging objective to oxidize these compounds efficiently and selectively under mild conditions.[1-12] In studies on oxidation catalysts, the reactivity of metal porphyrin complexes has aroused much interest because of their relation to cytochrome P-450, which oxidizes various

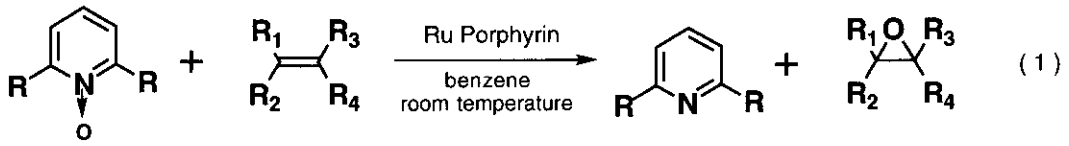
unreactive compounds under vital conditions[2]

In systems with metalloporphyrin catalysts, oxidants (X-O) such as peroxides, iodosylbenzene, OCl^- or aliphatic amine *N*-oxides are often used to convert low-valent metalloporphyrins (A) to high-valent metal-oxo complexes (B).[13] The typical reaction cycle was illustrated in Scheme 1. However, these oxidants themselves have moderate reactivity toward various substrates or are unstable and may cause side reactions or lowering of the selectivity in catalytic oxidations.[14] We tried to use heteroaromatic *N*-oxides, represented by pyridine *N*-oxide, as a new type of oxidants for metalloporphyrin-catalyzed oxidation systems.[15] In contrast to some of the oxidants in common use, heteroaromatic *N*-oxides do not have sufficient reactivity under the usual catalytic conditions either to oxidize substrates directly to undesirable side products, or to damage porphyrin catalysts and there by decrease the turnover number.[16] Moreover, they and their deoxygenated derivatives cannot be substrates for the catalytic oxidations, whereas iodosylbenzene and aliphatic amines (produced by the reduction of their *N*-oxides) are often oxidized instead of the intended substrates, so reducing the yields of reactions.[5c,17] However, heteroaromatic *N*-oxides had not previously been used as effective oxidants for reactions of this kind owing to their low oxidation abilities compared to the above oxidants

Scheme 1



In earlier communications, we reported that heteroaromatic *N*-oxides reacted as efficient oxidants for the ruthenium porphyrin-catalyzed oxidation of olefins (eq. 1).[18a-c] Olefins were converted into their epoxides with high selectivity using this system, and undesirable side reactions did not occur This system also possessed various other advantages as a reagent for epoxidation, such as mild conditions and easy overall procedures. However, alkanes or aliphatic alcohols were inert to oxidation with this system under the earlier conditions. We next examined the effect of additives upon the oxidation reactivity of this system, with the aim of developing a novel oxidation system for alkanes and other unreactive compounds based on this system. The activity of oxidation with some metalloporphyrin catalysts is known to be increased by the addition of certain



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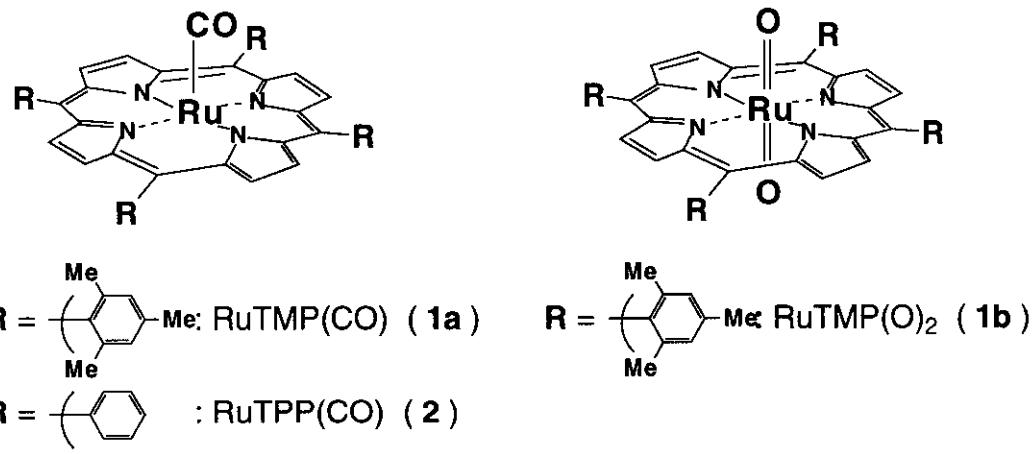
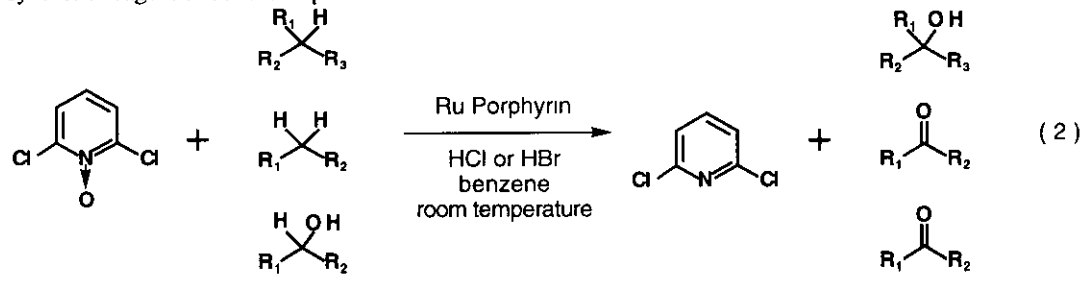


Scheme 2

compounds,[19,20] even though such enhancement has not been reported for the oxidation with ruthenium porphyrin catalysts. As reported recently in a communication, we found that the catalytic ability of ruthenium porphyrins was enhanced by the presence of a small amount of HCl or HBr and that the oxidation of alkanes or aliphatic alcohols with pyridine *N*-oxides was also catalyzed by ruthenium porphyrins with high efficiency in the presence of these acids (eq. 2).[18d] The system retained the various above-mentioned advantages as a synthetic reagent under the improved conditions.



(2)

As described above, our system is of great practical interest. However, the results were also interesting intellectually, because they revealed the unique reactivity of ruthenium porphyrin complexes to catalyze oxygen atom transfer reactions from rather weakly reactive compounds as oxidants to various substrates. Although many oxidation systems for olefins or alkanes with or without catalysts have been developed, only

photochemical reactions are effective for oxidation of olefins or alkanes using heteroaromatic *N*-oxides, other than our reactions.[21] Here we report the details of our work presented in the earlier communications, and the results of further studies to extend its scope.

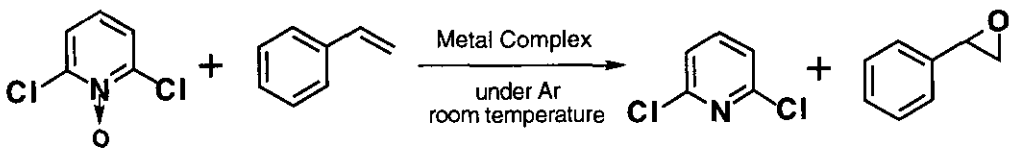
RESULTS AND DISCUSSION

The Epoxidation of Olefins with 2,6-Disubstituted Pyridine *N*-Oxides and Ruthenium Porphyrins

Some pyridines or other heteroaromatic compounds are known to coordinate with the metal atom of porphyrin complexes. Thus, the oxygen atom transfer reactions from 2,6-disubstituted pyridine *N*-oxides to olefins in the presence of various metalloporphyrin catalysts were investigated (eq. 3), because pyridines generated by the deoxygenation of these *N*-oxides were expected to be prevented from coordinating to the metal atom of the catalysts and inhibiting the catalytic reactions owing to the steric hindrance. As shown in Table 1, the oxidation of styrene (**5**) by 2,6-dichloropyridine *N*-oxide (**3f**) was efficiently catalyzed by ruthenium porphyrin complexes to afford styrene oxide with high selectivity. The reaction with $Ru^{VI}TMP(O)_2$ (**1b**)[22] proceeded most efficiently (Table I, Run 1). The substrate styrene was completely epoxidized by 2,6-dichloropyridine *N*-oxide in the presence of a catalytic amount of this catalyst within 2 h at room temperature.

		Yield[a]	
Run	Catalyst	Styrene oxide (**5**)[b]	2,6-diClpyridine (**4f**)[c]
1[d]	$RuTMP(O)_2$	100%	95%
2	RuTMP(CO)	99%	93%
3	RuTPP(CO)	26%	55%
4	$Ru(PPh_3)_3Cl_2$	n.d.[f]	n.d
5	$Ru(PPh_3)_4Cl_2$	n.d.	n.d.
6	FeTMPCl	n.d.	n.d.
7	MnTMPCl	n.d.	n.d.
8[e]	MnTDFPPCl	n.d.	n.d.
9	CoTPP	n.d.	n.d.
10	MoTMP(O)(OH)	n.d.	n d.
11	RhTMP(Cl)	n.d.	n.d.

Table I These reactions were carried out in benzene at room temperature under Ar overnight ([styrene] =170 mM, [2,6-diClpyridine *N*-oxide]=180 mM, [catalyst]=1 mM). a) Detected by glc. b) Based on styrene. c) Based on 2,6-dichloropyridine *N*-oxide d) Completed in 2 h . e) Carried out in CH_2Cl_2 f) Not detected.



(3f) (5) (4f) (6) (3)

This is the first time that a heteroaromatic *N*-oxide has been used as an efficient oxidant for metalloporphyrin-catalyzed oxidation systems and for catalytic olefin oxidation systems.[2,3,13,16]

The porphyrin complexes of Mn, Fe, Co, Mo, and Rh did not act as catalysts for this epoxidation (Runs 6-11), and neither did PPh_3 complexes of ruthenium (Runs 4,5). The reaction with $Ru^{II}TMP(CO)$ (**1a**)[22] also proceeded efficiently with an induction period (Run 2). However, the reaction with this catalyst did not proceed under a completely dark condition. Visible light may be needed to cleave the carbonyl-metal bond. $Ru^{II}TPP(CO)$ (**2**)[22] was less effective as a catalyst than the above two TMP complexes (Run 3). It was reported that unhindered TPP complexes of ruthenium form μ-oxo dimer type Ru-O-Ru.[23] $Ru^{II}TPP(CO)$ may be converted into the dimer under the catalytic conditions, leading to loss of the activity.

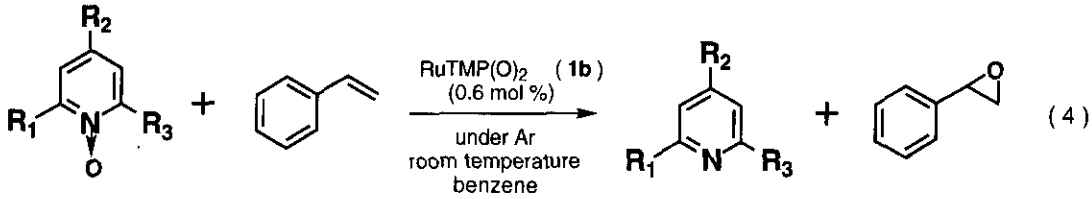
The oxygen transfer reactivities of various pyridine *N*-oxide derivatives were compared (eq. 4),[24] and the results are summarized in Table II. As expected, substituents at the 2 and 6 positions on the pyridine rings were necessary for high activity. 2-Mono-substituted pyridine *N*-oxides (Runs 2,3) had lower efficiency than the 2,6-disubstituted types (Runs 4-7) in terms of the rate of epoxidation and the yield of styrene oxide, and pyridine *N*-oxide had almost no activity (Run 1). The epoxidation of styrene with $RuTMP(O)_2$ (**1b**) and 2,6-lutidine *N*-oxide (**3c**) was carried out in the presence of pyridine (**4a**). Only 2 eq of pyridine with respect to

			Yield[a]		
Run	*Pyridine N-oxide*		Epoxide[b]	Pyridine[c]	Time
1	none	(**3a**)	trace	n.d.[d]	o.n.[e]
2	2-Me	(**3b**)	26%	n.d.	o.n.
3	2-Cl	(**3e**)	94%	100%	o.n.
4	2,6-diMe	(**3c**)	95%	n.d.	6h
5	2,4,6-triMe	(**3d**)	93%	95%	6h
6	2,6-diCl	(**3f**)	100%	95%	2h
7	2,6-diBr	(**3g**)	98%	100%	6h
8	2,6-diPh	(**3h**)	trace	n.d.	o.n.

Table II These reactions were carried out in benzene at room temperature under Ar([olefin]=170 mM, [pyridine *N*-oxide]=180 mM, $[RuTMP(O)_2]$=1 mM) a) Detected by glc. b) Based on olefins. c) Based on pyridine *N*-oxides. d) Not determined. e) Overnight (16~20 h).

the catalyst almost completely inhibited the catalytic reaction. Thus, this difference in reactivity may arise from

the difference in coordination ability of pyridines formed by the oxygen transfer reaction In the case of pyridine *N*-oxide (**3a**), pyridine coordinates strongly with the ruthenium atom, causing inhibition of the catalytic activity of Ru porphyrin, whereas the 2,6-disubstituted pyridines do not coordinate. Interestingly, 2,6-diphenylpyridine *N*-oxide (**3h**) was not an effective oxidant for this system (Run 8). It is probable that excessively large substituents interfere with the interaction between the oxygen atom of *N*-oxides and the metal.



(4)

$R_1 = R_2 = R_3 = H$: **3a** (**5**)
R_1 = Me, $R_2 = R_3 = H$: **3b**
$R_1 = R_3$ = Me, $R_2 = H$: **3c**
$R_1 = R_2 = R_3$ = Me : **3d**
R_1 = Cl, $R_2 = R_3 = H$: **3e**
$R_1 = R_3$ = Cl, $R_2 = H$: **3f**
$R_1 = R_3$ = Br, $R_2 = H$: **3g**
$R_1 = R_3$ = Ph, $R_2 = H$: **3h**

$R_1 = R_2 = R_3 = H$: **4a** (**6**)
R_1 = Me, $R_2 = R_3 = H$: **4b**
$R_1 = R_3$ = Me, $R_2 = H$: **4c**
$R_1 = R_2 = R_3$ = Me : **4d**
R_1 = Cl, $R_2 = R_3 = H$: **4e**
$R_1 = R_3$ = Cl, $R_2 = H$: **4f**
$R_1 = R_3$ = Br, $R_2 = H$: **4g**
$R_1 = R_3$ = Ph, $R_2 = H$: **4h**

Chloro-substituted pyridine *N*-oxides proved to be more effective than the methyl-substituted ones. For example, when collidine *N*-oxide (**3d**) was used as the oxidant with $RuTMP(O)_2$ (**1b**), it took 6 h to complete the reaction (Run 5), while in the case of 2,6-dichloropyridine *N*-oxide (**3f**), it took only 2 h (Run 6). We think that the high efficiency in the latter case arises partly because the chloro substituents reduce the electron density of the pyridine ring and weaken the oxygen-nitrogen bond of the *N*-oxide.

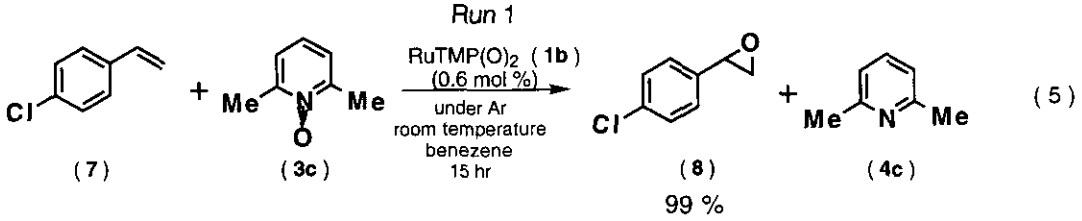
$Ru^{VI}TMP(O)_2$ (**1b**) was a less effective catalyst in CH_2Cl_2 than in benzene. The epoxidation of styrene with this catalyst and 2,6-dibromopyridine *N*-oxide (**3g**) in CH_2Cl_2 took almost 1 day to complete, while in benzene, it took 6 h. The reaction with 2,6-collidine *N*-oxide (**3d**) did not proceed efficiently in CH_2Cl_2, and about 60 % of the styrene remained intact after 1 day of reaction. Owing to its relatively strong coordination ability, CH_2Cl_2 may inhibit the catalytic reaction of ruthenium porphyrins by coordinating to the ruthenium atom.[25]

Several olefins were epoxidized with this system and the resulting epoxides were isolated (eq. 5,6) The yields are summarized in Table III. *p*-Chlorostyrene (**7**) and *cis*-stilbene (**11a**) were oxidized by lutidine *N*-oxide (**3c**) or collidine *N*-oxide (**3d**) in the presence of a catalytic amount of $Ru^{VI}TMP(O)_2$ (**1b**) to afford the epoxide selectively in satisfactory yield (99% and 98%, respectively) (eq 5). The *cis*-epoxide (**12a**) was obtained from *cis*-stilbene stereoretentively. Epoxidation of *p*-phenylstyrene (**9**) was accompanied by the

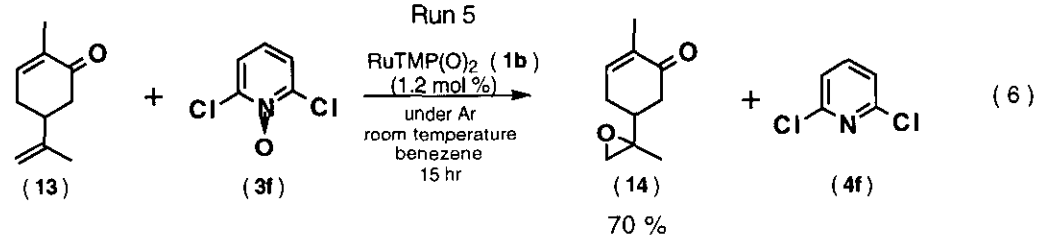
Run	Olefin		Pyridine *N*-oxides		Yield[a] (Epoxide)
1	*p*-chlorostyrene	(**7**)	2,6-diMe	(**3c**)	99%
2			2,4,6-triMe	(**3d**)	99%
3	*p*-phenylstyrene	(**9**)	2,4,6-triMe	(**3d**)	87%
4	*cis*-stilbene	(**11a**)	2,4,6-triMe	(**3d**)	98%[c]
5[b]	*l*-carvone	(**13**)	2,6-diCl	(**3f**)	70%[d]

Table III These reactions were carried out in benzene at room temperature under Ar overnight ([olefin]=170 mM, [pyridine *N*-oxides]=180 mM, [$RuTMP(O)_2$]=1 mM) a) Isolated yield (based on olefins) b) [$RuTMP(O)_2$]=2 mM. c) Yield of *cis*-epoxide. d) Yield of the terminal olefin epoxide

formation of *p*-phenylphenylacetaldehyde (y.< 5%). However, no aldehyde was detected in the oxidation of olefins tested other than *p*-phenylstyrene. Only the terminal olefin of *l*-carvone (**13**) was epoxidized and the α,β-unsaturated ketone group was unaffected under the conditions of Run 5 (eq. 6).



(5)



(6)

The pyridines generated by the reduction of their *N*-oxides were easily separated from the epoxides by silica gel column chromatography. Lutidine (**4c**) and collidine (**4d**) could also be separated from the resulting reaction mixtures by washing the mixtures with weak acid, which did not affect the epoxides.

Selective Epoxidation between Olefins

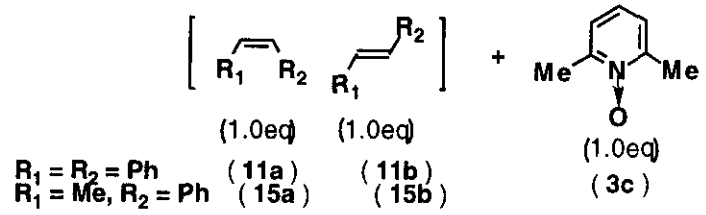
The present reagent system offers the advantages of high chemo-selectivity, mild conditions and simple handling procedures. Moreover, 2,6-disubstituted pyridine *N*-oxides are readily available, and safe to handle. Ruthenium porphyrins can also be prepared easily, can be stored for months with almost no decomposition, and are only needed in small amounts. In the epoxidation of norbornene with $Ru^{VI}TMP(O)_2$ (**1b**), the turnover number reached 16500. Therefore, we investigated whether our system showed several remarkable

selectivities which are known to occur in epoxidations catalyzed by porphyrins having bulky substituents on their rings.[19a,26,27]

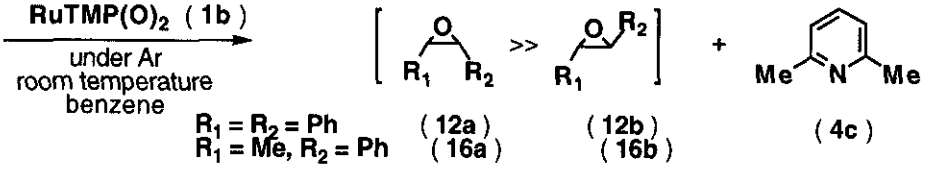
Run	Olefin	Yield (Epoxide) *cis*	*trans*	*cis* / *trans*
1	stilbene (*cis* (**11a**) : *trans* (**11b**) = 1:1 mixture)	87 %[b,i]	1 %[c,f]	87
2	*β*-methylstyrene (*cis* (**15a**) : *trans* (**15b**) = 1:1 mixture)	89 %[b,g]	5 %[c,g]	18
3[a]	*trans,cis,trans*-1,5,9-cyclododecatriene (**17**)	40 %[d,g]	8 %[e,g]	10[h]

Table IV These reactions were carried out in benzene at room temperature under Ar overnight ([*cis*-olefin]=[*trans*-olefin]=[lutidine *N*-oxide]=170 mM, [RuTMP(O)$_2$]=1 mM) a) [cyclododecatriene] =170 mM, [lutidine *N*-oxide]=180 mM, [RuTMP(O)$_2$]=4 mM. b) Based on *cis*-olefins. c) Based on *trans*-olefins. d) Yield of 5,6-epoxide based on cyclododecatriene. e) Yield of 1,2-epoxide based on cyclododecatriene f) Detected by glc. g) Determined by 400 MHz nmr after partial purification. h) Corrected ratio of products accounting for two *trans* double bonds and one *cis* double bond.

Table IV presents results for the competitive epoxidation of *cis*- and *trans*-olefins using this system. A mixture of *cis*- (**11a**) and *trans*-stilbene (**11b**) (170 mM each) reacted with 2,6-lutidine *N*-oxide (**3c**) (170 mM) in the presence of a catalytic amount of RuTMP(O)$_2$ (**1b**) (1 mM) to afford *cis*-stilbene oxide (**12a**) in an 87% yield based on *cis*-stilbene used, but only 1% of *trans*-stilbene (**12b**) was converted into its epoxide (Run 1, eq. 7). The epoxidation of *trans*-stilbene alone proceeded stereoretentively, like that of *cis*-stilbene, in a 7% yield. The competitive epoxidation of *cis*- (**15a**) and *trans*-*β*-methylstyrene (**15b**) under the same conditions proceeded with similar results (Run 2). The reaction of *trans,cis,trans*-1,5,9-cyclododecatriene (**17**) with this system also showed that *cis*-olefin was more highly reactive than *trans*-olefin (Run 3).[28]



(7)

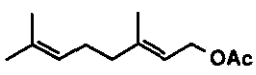


Some terpenes in their acetate form were epoxidized using this system to give the results summarized in Table V (Scheme 3). In all cases, the 6,7-double bonds were selectively epoxidized. The steric and electronic effects of acetoxy groups may cause the highly selective epoxidation.

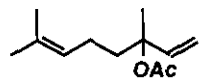
The Reactivity of Other Heteroaromatic *N*-Oxides as the Oxidants

We next examined the ability of other heteroaromatic *N*-oxides, which are as stable as pyridine *N*-oxides, to act

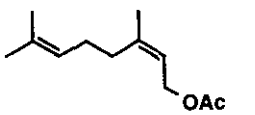
Scheme 3



geranyl acetate (**19a**)



linalyl acetate (**19c**)



neryl acetate (**19b**)

1,5,9-cyclododecatriene (**17**)

Run	Terpenes		Yield[a] 6,7-Epoxide	2,3-Epoxide	Diepoxide
1	geranyl acetate	(**19a**)	79%[b] (90%)[c]	1% (1%)	3% (3%)
2	neryl acetate	(**19b**)	75% (78%)	2% (2%)	16% (17%)
3	linalyl acetate	(**19c**)	97% (97%)	0%[d] (0%)	0% (0%)

Table V *These reactions were carried out in benzene at room temperature under Ar for 2 days ([terpene]=170 mM, [lutidine N-oxide]=250 mM, [RuTMP(O)$_2$]=1 mM).* a) Determined by 400 MHz nmr b) Based on terpenes. c) Based on conversion d) 1,2-Epoxide.

as oxidants for the epoxidation catalyzed by ruthenium porphyrin.[29] A variety of heteroaromatic *N*-oxides were allowed to react with styrene (**5**) in the presence of a catalytic amount of RuTMP(O)$_2$ (**1b**), as summarized in Table VI. The *N*-oxides of 2,3,5,6-tetramethylpyrazine (**37**) (**38**), acridine (**48**), 2-methylquinoline (**46**), 4-nitroquinoline (**44**), and 3,6-dichloropyridazine (**40**) act as oxidants in this catalytic reaction (Runs 1-6). In particular, with the *N*-oxides of 2,3,5,6-tetramethylpyrazine or 4-nitroquinoline, styrene was quantitatively converted into the epoxide. But 4,6-dimethyltriazine *N*-oxide (**42**) was inactive (Run 7). This difference in reactivity may arise because in the last case the resulting base, 4,6-dimethyltriazine, coordinates strongly with porphyrin metal to inhibit the catalytic activity of ruthenium porphyrin. We considered that not only pyridine *N*-oxides but also other heteroaromatic *N*-oxides could act as oxidants in this system when their deoxygenated compounds could not coordinate strongly with the metal because of the steric hindrance of substituents on their rings. It seems likely that the electron-withdrawing nitro substituent activated 4-nitroquinoline *N*-oxide (**44**) as an oxidant.

The Oxidation of Alcohols and Sulfides

Substrates other than olefins were also oxidized with RuTMP(O)$_2$ and lutidine *N*-oxide. The results for the

oxidation of alcohols are summarized in Table VII. Allyl alcohols were oxidized by lutidine *N*-oxide (**3c**) in the presence of $RuTMP(O)_2$ (**1b**) to afford α,β-unsaturated aldehydes selectively, and the resulting aldehydes were isolated (Runs 2,3). The reaction of benzyl alcohol (**23**) also proceeded efficiently (Run 1) but that of 2-phenylethanol (**29**) did not (Run 4). Table VIII shows the results for the oxidation of sulfides under a variety of conditions (eq. 9). The oxygen transfer reaction from lutidine *N*-oxide (**3c**) to phenyl methyl sulfide (**31**) in the presence of $RuTMP(O)_2$ (**1b**) did not proceed as efficiently as the oxidation of olefins or alcohols at room temperature, and it required 6 days for the complete consumption of the starting sulfide (Run 2).

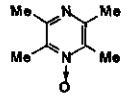
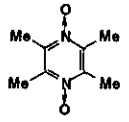
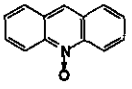
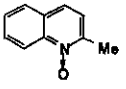
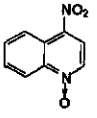
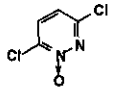
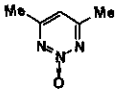
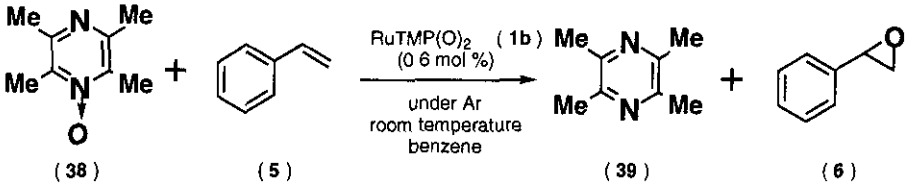
Run	Oxidant		Yield[b] Styrene oxide[c]	Reduced oxidant[d]
1		(**38**)	100 %	100 %
2[a]		(**37**)	99 %	100 %
3		(**48**)	59 % (87 %)[e]	n.d.[f]
4		(**46**)	46 % (86 %)	42 %
5		(**44**)	99 %	n.d.
6		(**40**)	28 %	n.d.
7		(**42**)	trace	n.d.

Table VI These reactions were carried out in benzene at room temperature under Ar for 1 day ([styrene]=170 mM, [N-oxide]=180 mM, [$RuTMP(O)_2$] =1 mM). a) [*N*-oxide]=90 mM. b) Yields were detected by glc. c) Based on styrene d) Based on *N*-oxide e) Based on conversion f) Not determined



(**38**) (**5**) (**39**) (**6**) (8)

However, in refluxing benzene, the sulfide was exhausted within half an hour to afford mainly the sulfoxide

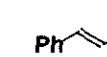
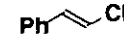
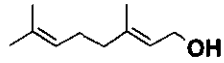
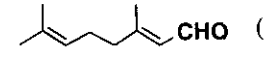
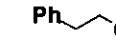
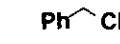
Run	Substrate		Yield[a]	Product	
1		(**23**)	81 %[d]	PhCHO	(**24**)
2		(**25**)	79 %[c] (87 %)[b]		(**26**)
3		(**27**)	45 %[c] (65%)		(**28**)
4		(**29**)	2 %[d]		(**30**)

Table VII These reactions were carried out in benzene at room temperature under Ar overnight ([substrate] =170 mM, [lutidine *N*-oxide]=170 mM, [RuTMP(O)$_2$]=1 mM). a) Based on substrate. b) Based on conversion. c) Isolated yield. d) Determined by glc.

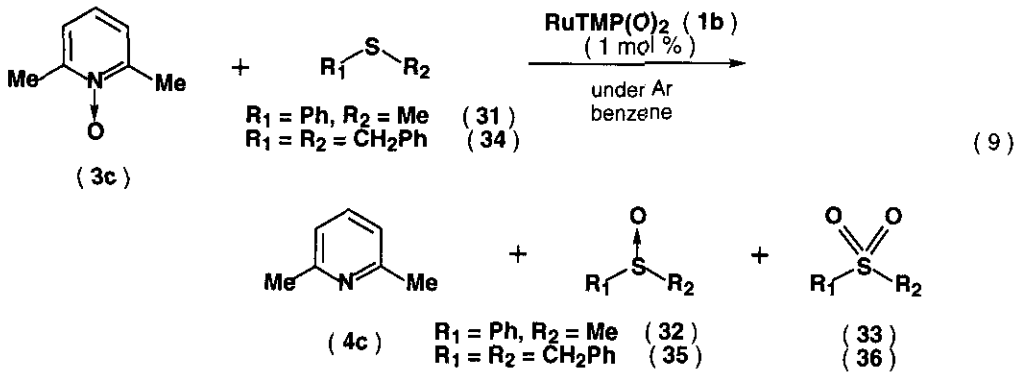
Run	Sulfides	Catalysts	Conditions		Yield[a] Sulfoxide	Sulfone
1	phenyl methyl sulfide (**31**)	RuTMP(O)$_2$	reflux	0.5h	90%[b]	7%[b]
2		RuTMP(O)$_2$	room temperature	6d	85%	2%
3		Ru(PPh$_3$)$_4$Cl$_2$	reflux	4h	80%	4%
4		none	reflux	10h	4%	2%
5	benzyl sulfide (**34**)	RuTMP(O)$_2$	reflux	2h	94%[c]	3%[c]

Table VIII These reactions were carried out in benzene under Ar ([sulfide]=200 mM, [lutidine *N*-oxide] =200mM, [RuTMP(O)$_2$]=2 mM). a) Based on sulfide. b) Determined by glc. c) Isolated yield.

(**32**) (Run 1). Heating the solution (80°C) forced the reaction catalyzed by Ru(PPh$_3$)$_4$Cl$_2$ to proceed as well, but it took 4 h for completion (Run 3). The rate of oxidation of benzyl sulfide (**34**) was slower than that of phenyl methyl sulfide (**31**) under the same conditions (Run 5). The competitive reaction of benzyl sulfide (**34**) and phenyl methyl sulfide (**31**) was examined, but the reaction proceeded as slowly as did the oxidation of benzyl sulfide alone, and benzyl sulfide was more reactive than phenyl methyl sulfide (the ratio of the resulting sulfoxides: benzyl sulfoxide (**35**) / phenyl methyl sulfoxide (**32**) ≈ 6 / 4). The hypothesis that sulfides or the resulting sulfoxides coordinate with porphyrin metal to inhibit the catalytic reaction competitively and that benzyl sulfide or its sulfoxide can coordinate more strongly than phenyl methyl sulfide or its sulfoxide, can account for these reactivities of the sulfides.

The Oxidation of Alkanes and Aliphatic alcohols in the Presence of HCl or HBr

One of the most attractive objectives in the field of catalytic oxidation chemistry is to develop systems with which alkanes or other low-reactive compounds can be oxidized efficiently and selectively.[1] However, ruthenium porphyrins showed almost no catalytic reactivity for the oxygen transfer reactions from pyridine *N*-oxides to alkanes under the above conditions. Next, we investigated the effect of additives upon the oxidation



(9)

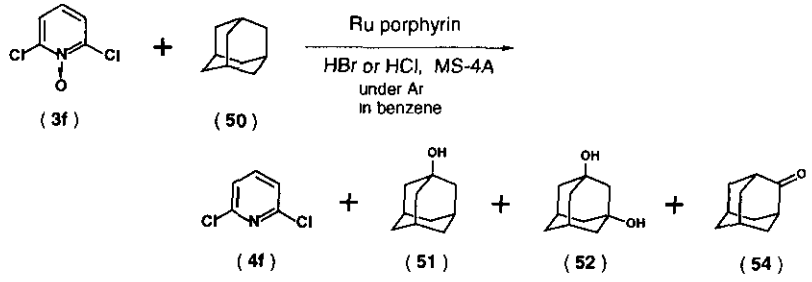
reactivity of this system, because in some metalloporphyrin-catalyzed oxidation systems, the reactivity is known to be enhanced by the addition of certain compounds.[19,20] For example, addition of imidazole enhances the oxidation reactivity with Mn porphyrins.[4e,4f,4j,19a] In these reactions, imidazole is considered to coordinate as the axial ligand to activate the catalytic reactivity of Mn porphyrin. Some carboxylic acids are also known to be effective additives for the oxidation catalyzed by Mn porphyrin.[4f] It was indicated that these acids accelerate the formation of high-valent active intermediates from oxidants and low-valent Mn porphyrins. We found that the catalytic ability of ruthenium porphyrins is enhanced by the presence of a small amount of HCl or HBr, and that, in the presence of these acids, the oxidation of alkanes with pyridine *N*-oxides is also catalyzed by ruthenium porphyrins with high efficiency.[30] The results for the oxidation of adamantane under

Run	Catalyst	Additive	Time	Temp.	Products, % yield[a),b)]		
					(**51**)	(**52**)	(**54**)[i)]
1	$RuTMP(O)_2$	HCl	24h	room temperature	68	25	1
2	$RuTMP(O)_2$	HBr	24h	room temperature	63	15	2
3	$RuTMP(O)_2$	–	24h	room temperature	4	n.d.[f)]	trace[g)]
4	–	HCl	24h	room temperature	1	n d.	n.d.
5	RuTMP(CO)	HBr	24h	room temperature	64	20	2
6	RuTPP(CO)	HBr	6h	room temperature	66	27	trace
7	$RuCl_2(PPh_3)_4$	HBr	24h	room temperature	trace	n.d.	n.d.
8[c),d)]	RuTPP(CO)	HBr	15h	40°C	66 (6600)[h)]	22 (4400)	0.5 (100)
9[c),e)]	RuTPP(CO)	HBr	6days	40°C	69 (69000)	25 (50000)	0.5 (1000)
10[c),e)]	RuTPP(CO)	HBr	6h	80°C	59 (59000)	29 (58000)	1.5 (3000)
11[c)]	–	HBr	6h	80°C	1	n.d.	n.d.

Table IX These reactions were carried out in benzene under Ar. The reaction mixtures contained adamantane (200 mM), 2,6-dichloropyridine *N*-oxide (260 mM), catalyst (1.0 mM), 36% HCl aq. (20~40 ml/l : 200~410 mM) or 48% aq. HBr (20~40 ml/l : 120~240 mM), and molecular sieves 4A (100 g/l). a) Yields were based on starting adamantane (%). b) Determined by glc. c) [adamantane]=1.0 M, [*N*-oxide]=1.3 M. d) [catalyst]=100 μM. e) [catalyst]=10 μM. f) Not detected. g) <0.5%. h) The turnover number per catalyst (turns). i) Adamantan-2-ol was not detected.

several conditions are summarized in Table IX (eq. 10). We first used 2,6-dichloropyridine *N*-oxide (**3f**) as

the oxidant and $RuTMP(O)_2$ (**1b**) as the catalyst, because they were the reagents of choice for the epoxidation. As shown in Run 3, only a 4 % yield of oxidation products was obtained in the oxidation of adamantane (**50**) with 2,6-dichloropyridine *N*-oxide and $RuTMP(O)_2$, and most of the adamantane remained intact after the reaction for 24 h. In contrast, the reaction proceeded efficiently after the addition of a small amount of conc. HCl and molecular sieves 4A. Under this condition, almost all of the adamantane was consumed to afford adamantan-1-ol (**51**), adamantane-1,3-diol (**52**), and adamantan-2-one (**54**) in yields of 68 %, 25 %, and 1 % based on adamantane, respectively (Run 1). Adamantane was also efficiently oxidized in the presence of HBr instead of HCl (Run 2). In these reactions, halogenated compounds, such as 1-bromoadamantane, were not detected. The reaction did not proceed efficiently without the addition of molecular sieves Water may inhibit the reaction, because the addition of an anhydrous HCl solution of benzene was effective in the absence of these sieves, as described later.



(10)

The carbonyl complexes of ruthenium porphyrins were also effective catalysts for the reactions in the presence of HBr (Runs 5,6). In contrast to the above-described epoxidation with carbonyl complexes in the absence of HCl or HBr, the reactions with HBr proceeded efficiently in the dark. The carbonyl complexes of ruthenium porphyrins may be converted into the appropriate catalytic complexes by reaction with HBr. Interestingly, RuTPP(CO) (**2**) worked most efficiently among the catalysts described here. The reaction with this catalyst was completed within 6 h at room temperature (Run 6). As discussed below, Cl^- or Br^- appears to coordinate to the ruthenium porphyrins as an axial ligand under the catalytic conditions with HCl or HBr. Then, TPP complexes of ruthenium are presumably prevented from forming the μ-oxo dimer.[31] Without the loss of activity resulting from dimer formation, RuTPP(CO) is expected to react as a superior catalyst because of the reduced steric hindrance. It should be noted that the reactions with the above two carbonyl complexes of ruthenium porphyrins were efficiently enhanced by the addition of HBr, but not HCl.

Ruthenium catalysts were extremely stable under these conditions. Adamantane (**50**) was treated with 2,6-dichloropyridine *N*-oxide (**3f**) in the presence of 1.0×10^{-4} eq. of RuTPP(CO) (**2**) and HBr at 40°C. The oxidant was almost exhausted in 15 h, at which time the turnover number was 11100 (Run 8). With 1.0×10^{-5} eq. of catalyst, the turnover number reached 120000, even though it took 6 days to complete the reaction at 40°C (Run 9). At higher temperature, RuTPP(CO) gave a turnover number of 120000 during 6 h (Run 10). The turnover frequency for the last case was 5.6/s. In these reactions, almost all of the reagents, both *N*-oxide

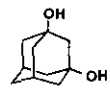
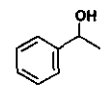
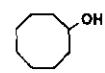
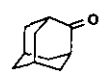
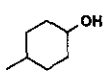
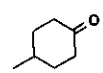
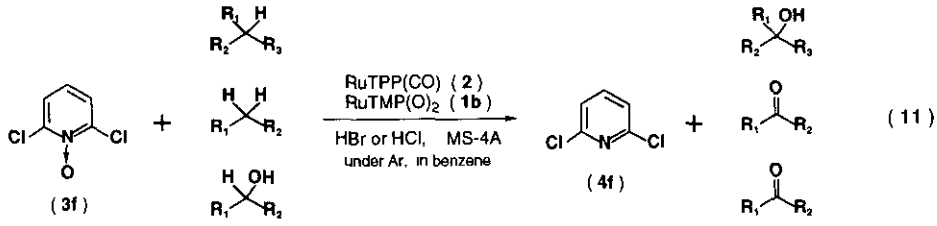
Run	Substrate		Condition	Product (Yields are based on substrates)[a]					
1		(**55**)	cat = RuTPP(CO) add = HBr [*N*-oxide] = 400 mM room temperature, 6 h		(**56**)	94 %		(2- : **58a** 3- : **58b** 4- **58c**)	trace[d]
2		(**55**)	cat = $RuTMP(O)_2$ add = HBr [*N*-oxide] = 440 mM 40°C, 9 h		(**56**)	77 %		(2- : **58a** 3- : **58b** 4- **58c**)	2- : 3 % 3- : 2 % 4- : 1 %
3		(**51**)	cat. = $RuTMP(O)_2$ add = HBr [*N*-oxide] = 220 mM 60°C, 4 h		(**52**)	74 %[b] (90 %[c])			
4		(**59a**)	cat = RuTPP(CO) add = HBr [*N*-oxide] = 240 mM room temperature, 6 h		(**60a**)	72 %[b] (80 %[c])			
5		(**61**)	cat = $RuTMP(O)_2$ add. = HCl [*N*-oxide] = 440 mM room temperature, 24 h		(**63**)	88 %		(**62**)	n.d.[e]
6		(**64**)	cat = RuTPP(CO) add = HBr [*N*-oxide] = 600 mM room temperature, 40 h		(**66**)	77 %		(**65**)	2 %
7		(**67**)	cat = $RuTMP(O)_2$ add = HCl [*N*-oxide] = 220 mM room temperature, 24 h		(**68**)	88 %			
8		(**53**)	cat = $RuTMP(O)_2$ add. = HBr [*N*-oxide] = 220 mM room temperature, 24 h		(**54**)	84 %[b]			
9		(**57c**)	cat. = $RuTMP(O)_2$ add = HCl [*N*-oxide] = 220 mM room temperature, 24 h		(**58c**)	81 %[b]			

Table X These reactions were carried out under Ar in benzene ([substrate]=200 mM, [catalyst]=1 mM, aq. HBr (47%) or aq. HCl (36%) = 30 ml/l, molecular sieves 4A = 100 g/l) a) Yields are based on substrates (detected by glc) b) Isolated yield c) Based on conversion d) <0.5% e) Not detected

and adamantane, were consumed at the end of the reaction, so presumably the raction would have continued if further amounts of these reagents had been added to the resulting mixture.

Several alkanes were oxidized with this system (eq. 11). The results are shown in Table X. 1-Methylcyclohexanol (**56**) was selectively obtained with high efficiency in the oxidation of methylcyclohexane

(**55**) (y. 94 %) (Run 1). The oxidation of *cis*-decalin (**59a**) proceeded efficiently and *cis*-decalol (**60a**) was isolated in 72% yield (Run 4). The stereo isomer *trans*-decalol (**60b**) was not detected by glc analysis. Ethylbenzene (**61**) was converted into acetophenone (**63**) in 88 % yield (Run 5). Cyclooctane (**64**), which is less reactive than tertiary alkane or benzyl alkane, was oxidized to afford cyclooctanone (**66**) in reasonable yield (y. 77 %) (Run 6). It should be noted that the oxidation with RuTPP(CO) (**2**) proceeded more efficiently than the oxidation with $RuTMP(O)_2$ (**1b**) or RuTMP(CO) (**1a**) in general (compare Runs 1 and 2), but RuTPP(CO) did not act as an efficient catalyst for the oxidation of ethylbenzene. The relatively stable radical of ethylbenzene may liberate and attack the *ortho*-proton on the phenyl ring of TPP. It is also likely that the radical reacts with nitrogen of the porphyrin ring to generate the stable *N*-alkyl complex in the case of the less sterically hindered TPP complex.[32]

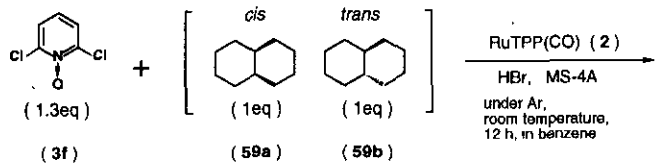


Aliphatic alcohols were also oxidized to afford the corresponding ketones (Runs 7~9), and some of the resulting ketones were isolated without difficulty. These results indicated that the ketones were generated *via* alcohols in the oxidation of secondary alkanes

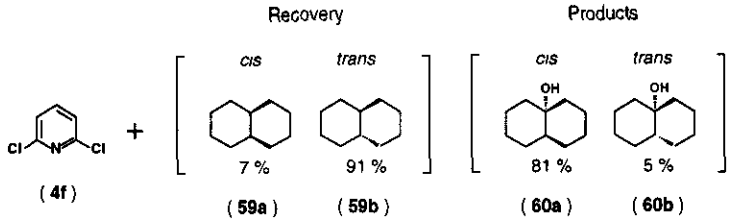
Competitive hydroxylation between *cis*- (**59a**) and *trans*-decalins (**59b**) was examined (eq. 12). An equimolar mixture of *cis*- and *trans*-decalin (200 mM each) was oxidized by *N*-oxide (260 mM) with RuTPP(CO) (**2**) to afford *cis*-decalol (**60a**) in 81 % yield and the *trans*-isomer (**60b**) in 5 % yield. The recoveries of *cis*- and *trans*-decalins were 7 % and 91 %, respectively The oxidation of *trans*-decalin alone proceeded efficiently to afford *trans*-decalol stereoretentively, similarly to the case of *cis*-decalin. Thus, the results showed that *cis*-decalin is much more reactive than *trans*-decalin as regards oxidation with this system. According to Balavoine et al.[33], the same selectivity was observed for competitive oxidation of decalins with other oxidation systems. In those reactions, *cis*-decalin was 10~12 times more reactive than *trans*-decalin. However, those reactions were carried out with excess substrate. In our oxidation, 20 times as much *cis*-decalol as *trans*-isomer was obtained under conditions such that over 90 % of *cis*-decalin was consumed.

Recently, some efficient alkane oxidation systems have been developed using manganese porphyrins.[4] The

systems with transition metal-substituted polyoxometalate catalysts[8] are also efficient. The reactions with Gif systems[10] proceed not only with high efficiency but also with unique selectivity. A high turnover number was reported in oxidation with the substituted bipyridyl complex of ruthenium.[7b] However, our system seems to be the most efficient in terms of turnover numbers and yields based on substrates among various metal-catalyzed alkane oxidation systems involving the activation of C-H bonds with a high-valent active intermediate.[1,2,4-10] As described above, heteroaromatic *N*-oxides have not been used as effective oxidants for the oxidation of olefins or alkanes without irradiation, except in our work.[21] The present results are



(12)



intellectually very interesting, because a highly efficient alkane oxidation system has been developed with highly stable compounds as oxidants. Moreover, this system offers various practical advantages for synthetic use, such as mild conditions, simple handling procedures, and the use of a stable and tractable oxidant.

Mechanistic Studies

In the catalytic reaction with cytochrome P-450, iron porphyrin oxo complexes are considered to be the active intermediates for the oxidation of substrates.[2] Since $RuTMP(O)_2$ (**1b**) was synthesized and characterized by Groves *et al.*[34], this complex has been regarded as an analogous complex to the active intermediate of cytochrome p-450, and the oxidation reactivity of this dioxo complex has attracted much interest.[34,36] Groves et al. also reported that $RuTMP(O)_2$ catalyzes the epoxidation of olefins with molecular oxygen in the absence of reductants.[34b,35,37] In their unique system, $RuTMP(O)_2$ has been considered to convert olefins into epoxides, and no other active intermediate which was more reactive than $RuTMP(O)_2$ was considered to be produced. It seemed that the *trans*-dioxo complex[38] could also be a candidate for the active intermediate for the reaction in our system. However, while the turnover number of their aerobic epoxidation is about 100 at most,

in our system using 2,6-disubstituted pyridine *N*-oxides as oxidants, ruthenium porphyrins work very efficiently as catalysts and the turnover number reached 16500 even in the epoxidation without HCl or HBr. Considering the difference in reactivity between the two systems, it seemed likely that some active intermediate other than $RuTMP(O)_2$ is generated during the oxidation with our system. We first investigated whether or not $RuTMP(O)_2$ could be the active intermediate in our oxidations, at least under the condition without HCl or HBr.

The rate constant of the reaction between $RuTMP(O)_2$ (**1b**) and 2-vinylnaphthalene (**69**) was determined for the mechanistic study. $RuTMP(O)_2$ (1 mM) was allowed to react with 2-vinylnaphthalene (100 mM) in benzene-d_6 under Ar at 30°C, and the 400 MHz ^{1}H-nmr spectra of this solution were measured at intervals. The pseudo first order rate constant, *k*, for the decrease of $RuTMP(O)_2$ was 0.22/min (see Figure 1). Next,

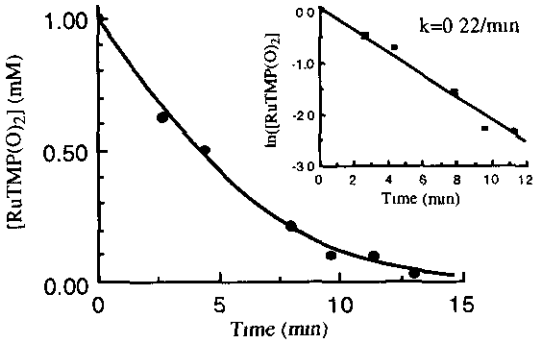


Figure 1 This reaction was carried out in benzene-d_6 at 30° under Ar ([vinylnaphthalene] = 100 mM, $[RuTMP(O)_2]$ = 1 mM).

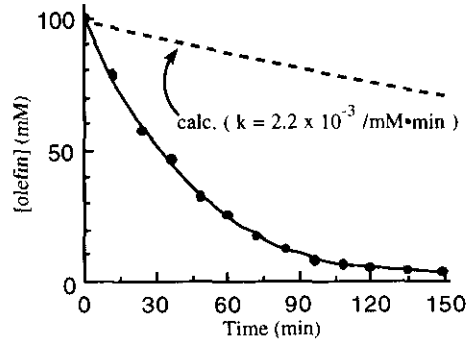
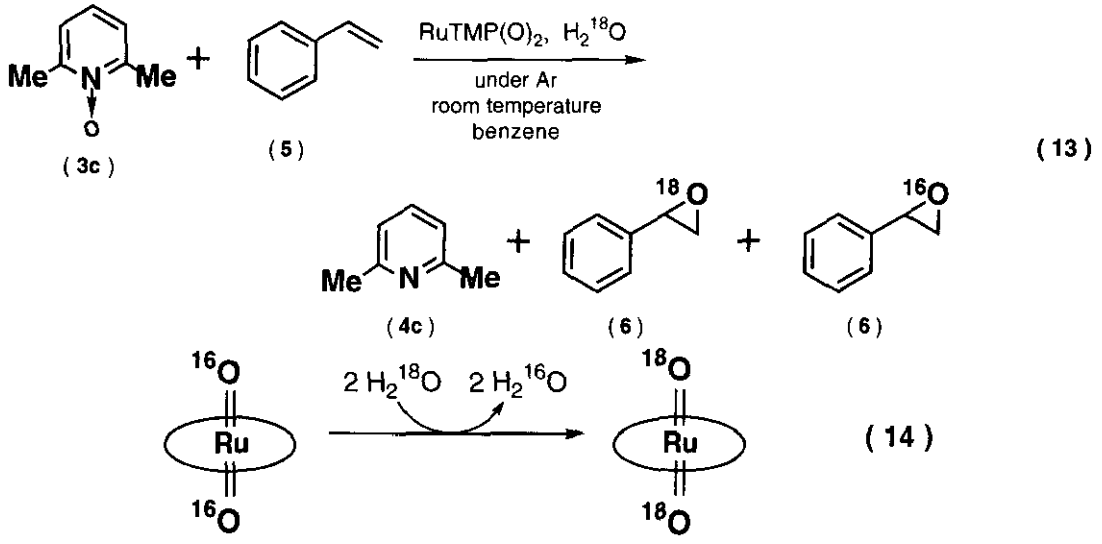


Figure 2 This reaction was carried out in benzene-d_6 at 30° under Ar ([vinylnaphthalene]=100 mM, [lutidine *N*-oxide]=100 mM, $[RuTMP(O)_2]$=1 mM)

the rate of catalytic epoxidation of 2-vinylnaphthalene (**69**) with $RuTMP(O)_2$ (**1b**) in the presence of 2,6-lutidine *N*-oxide (**3c**) was examined The reaction mixture and the conditions were the same as those for the above experiment, except that the mixture contained 100 mM 2,6-lutidine *N*-oxide in addition Figure 2 shows the concentration of vinylnaphthalene versus time curve for this epoxidation (solid line) It also shows the curve drawn by estimating the concentration of vinylnaphthalene during epoxidation based on the second order rate constant $k=2.2\times10^{-3}$/mM•min which was calculated from the above first order rate constant for the reaction between $RuTMP(O)_2$ and 2-vinylnaphthalene (dotted line). It is clear that the catalytic reaction proceeded at a much faster rate than was predicted from the reactivity of $RuTMP(O)_2$, which indicates that an active intermediate other than $RuTMP(O)_2$ mainly epoxidizes olefins during this catalytic reaction. The 6-valent *trans*-dioxo complexes of ruthenium porphyrins seem to be less reactive than the active intermediates in our

oxidations even under the condition without HCl or HBr.

A study on incorporation of ^{18}O from labeled water into the epoxide also supported the above proposal. The oxidation of styrene (**5**) with 2,6-lutidine *N*-oxide (**3c**) catalyzed by $RuTMP(O)_2$ (**1b**) was carried out by the presence of $H_2{}^{18}O$ (97% enriched) (eq. 13). The presence of water increased the amount of phenylacetaldehyde formed, but the main product remained the epoxide (**6**) (y. 84%), which showed a 27% incorporation of the ^{18}O label. Control experiments established that neither lutidine *N*-oxide nor styrene oxide underwent isotopic exchange with water under the catalytic conditions. The aerobic epoxidation of styrene was also examined in the presence of $H_2{}^{18}O$. The conditions were the same except that the reaction mixture did not contain lutidine *N*-oxide and was stirred under an oxygen atmosphere. An 81% ^{18}O incorporation from water ($H_2{}^{18}O$) into the resulting epoxide (y. 74%) was observed for this aerobic oxidation. We have suggested that such differences can be accommodated if the active intermediates for these two systems (*N*-oxide and aerobic) are different. It is known that oxygen atoms of oxo-metal complexes such as $RuTMP(O)_2$ readily exchange with that of water.[39,12a] We revealed that $RuTMP(O)_2$ was also converted into $RuTMP(^{18}O)_2$ in the presence of excess amount of $H_2{}^{18}O$ (eq. 14) [40] During the aerobic epoxidation $RuTMP(O)_2$ was supposed to undergo isotopic exchange prior to the oxidation of olefins; thus significant incorporation of ^{18}O into the resulting epoxide was observed In our system, another intermediate which is likely to be less attacked by water than $RuTMP(O)_2$ seems to be generated and to epoxidize olefins. However, it cannot be excluded that $RuTMP(O)_2$ may be regenerated under our conditions and be partly responsible for the epoxidation of olefins.[42]



The real intermediate in the reactions under conditions without HCl or HBr other than $RuTMP(O)_2$ remains

undetermined, but it is probably another metal-oxo species as inferred from previous reports on oxidation with Cr, Mn or group VIII metal catalysts.[3,13] We think that the oxidation reactivity of $RuTMP(O)_2$ may be activated by interacting with pyridine *N*-oxides. The dipolarity of *N*-oxides seems to be able to affect the character of the Ru-oxo bonds. We presume that pyridine *N*-oxides not only react as oxidants for the catalytic reactions, but also play a part in the formation of the active intermediate.[43-46] As described above, the reactions in our system were disturbed or accelerated by the addition of small amounts of certain compounds such as pyridine or HCl. Thus, it may be necessary for understanding the mechanism of our reactions under the condition without HCl or HBr to consider the effect of unexpected contaminants or by-products.[47]

In contrast, it might be possible to understand the mechanism under the condition with HCl or HBr by considering only the effect of these acids, because the acids greatly affected the reactivity of the catalytic oxidation, so that the influence of *N*-oxides other than the oxidants or other unexpected factors might become negligible.

To elucidate the effect of HCl, $RuTMP(O)_2$ (**1b**) was allowed to react with HCl without substrate or oxidant, and the resulting ruthenium porphyrin complex (**I**) was isolated (y. 82 %). The reaction conditions were the same as for the catalytic oxidations described above (Table 9 Run 1) except that the mixture did not contain substrate or oxidant. In the 400 MHz ^{1}H-nmr spectrum of **I**, peaks at -54.65 ppm and 12.49 ppm were observed. It was reported that $RuTPP(Cl)_2$ was obtained by the reaction of $(RuTPP)_2$ with HCl, and displayed peaks at -57.72 ppm and 11.52 ppm in its ^{1}H-nmr spectrum due to pyrrole proton and *meta*-proton, respectively.[48] Thus, **I** may be the *trans*-dichloro complex of ruthenium porphyrin, formulated as $RuTMP(Cl)_2$.

The catalytic abilities of a series of complexes, **I**, $RuTMP(O)_2$ (**1b**), and RuTMP(CO) (**1a**), were compared in the absence of HCl or HBr at 40°. As shown in Figure 3, **I** was the most efficient catalyst among them, suggesting that $RuTMP(O)_2$ and RuTMP(CO) acted as efficient catalysts after conversion into **I** or into complexes which could be generated more easily from **I** than from $RuTMP(O)_2$ or RuTMP(CO). However, the oxidation with $RuTMP(O)_2$ in the presence of HCl at 40°C proceeded far more efficiently than that with **I** in the absence of acid, and the amount of added HCl affected the efficiency of the oxidations (Figure 4). It should be noted that, in the reactions for Figure 4, a certain amount of anhydrous HCl solution of benzene was added and molecular sieves were not used. A reasonable hypothesis based on the above results is as follows. HCl or HBr first converts the dioxo or CO complexes of ruthenium porphyrins into the Cl^- or Br^- ligand

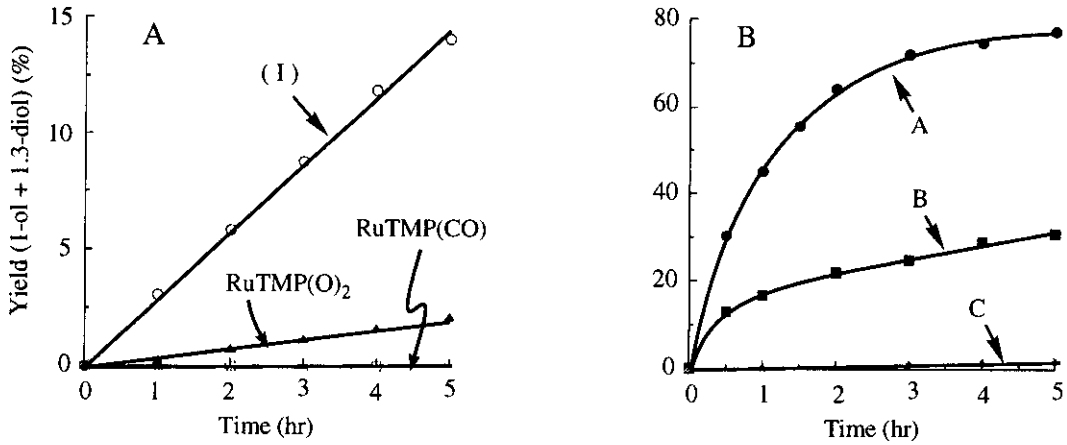
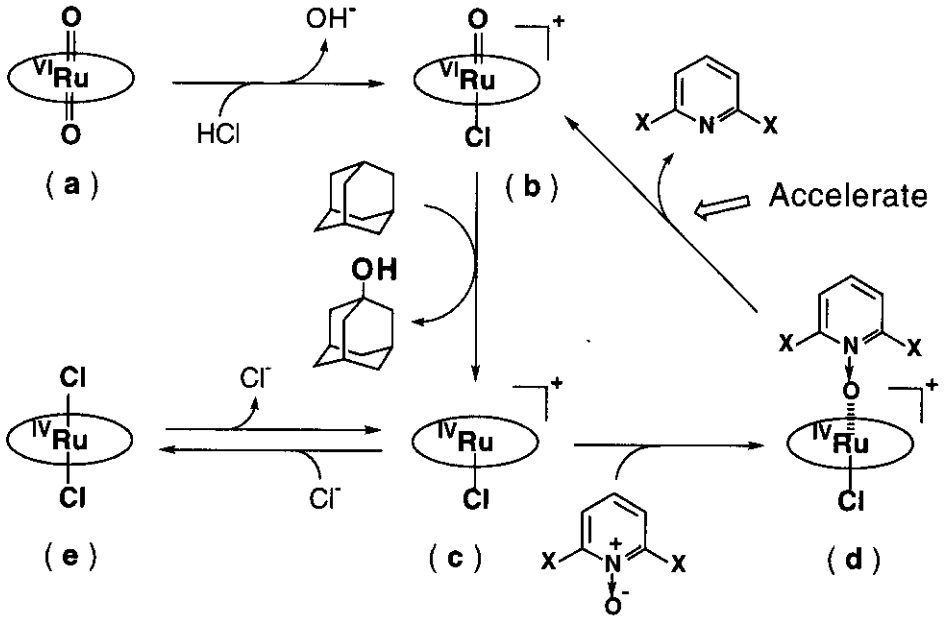


Figure 3 (A) The hydroxylation of adamantane with 2,6-dichloropyridine *N*-oxide catalyzed by RuTMP(Cl)$_2$, RuTMP(O)$_2$, and RuTMP(CO). These reactions were carried out in benzene under Ar at 40°C ([adamantane]=[2,6-dichloropyridine *N*-oxide]=100 mM, [catalyst]=0.4 mM). Neither HCl (or HBr) nor molecular sieves was added to the reaction mixtures. Yields (based on starting adamantane) were determined by glc.

Figure 4 (B) The hydroxylation of adamantane with 2,6-dichloropyridine *N*-oxide catalyzed by RuTMP(O)$_2$ in the presence or the absence of HCl. These reactions were carried out in benzene under Ar at 40°C ([adamantane]=[2,6-dichloropyridine *N*-oxide]=100 mM, [RuTMP(O)$_2$] =0 4 mM). A saturated HCl solution of benzene was added to these reaction mixtures (A : 10 ml/l, B . 5 ml/l, C · 0 ml/l). Molecular sieves were not added to the mixture, because the added HCl solution was anhydrous Yields (based on starting adamantane) were determined by glc



Scheme 4

complexes. The active intermediates are the ruthenium porphyrin oxo complexes formulated as $[Ru^{VI}(por)(X)(O)]^+$ (X=Cl or Br) (b), and the acids accelerate the formation of the Ru-oxo intermediate from *N*-oxide and ruthenium porphyrin in reduced form (Scheme 4).[49,50] The present results do not allow us to identify the mechanism or the active intermediate. Nevertheless, the catalytic activity of ruthenium porphyrins appears to be influenced drastically by the nature of the axial ligands. Further investigation of the mechanistic details is needed and is in progress in our laboratory.

CONCLUSION

Ruthenium porphyrins efficiently catalyzed the oxygen atom transfer reactions from various heteroaromatic *N*-oxides to olefins, allyl or benzyl alcohols and sulfides. The catalytic activity of ruthenium porphyrin complexes was enhanced by the addition of a small amount of HCl or HBr. In the presence of these acids, the oxidations of alkanes or aliphatic alcohols with 2,6-dichloropyridine *N*-oxides were also efficiently catalyzed by ruthenium porphyrin complexes. With this system, olefins were converted into epoxides with high selectivity, and alkanes were also selectively converted into alcohols or ketones. Heteroaromatic *N*-oxides are very stable compounds, and the present system is the first that is able to use these *N*-oxides as oxidants for the oxidations of olefins or alkanes, except for photochemical reactions. Nevertheless, the oxidations of various substrates, even alkanes, with this system proceeded in good yields. Moreover, ruthenium porphyrins work very efficiently as catalysts, in the hydroxylation of adamantane, the turnover number reaching 120000. This system should be valuable for synthetic purposes, because it possesses practical advantages, such as mild conditions, tractability of oxidants and easy overall procedures.

To elucidate the active intermediate in these reactions, the reactivities of ruthenium porphyrin *trans*-dioxo complexes were examined These complexes, while quite stable, were regarded as active intermediates for the ruthenium porphyrin-catalyzed epoxidation of olefins with molecular oxygen. However, the *trans*-dioxo complexes were less active than the main active intermediate for our oxidations with pyridine *N*-oxides. In the case of the reactions with HCl or HBr, we speculated that these acids plays two roles for the enhancement of the reactions: the first is to convert the dioxo or CO complexes of ruthenium porphyrins into Cl^- or Br^- coordinated complexes, and the second is to accelerate the deoxygenation of *N*-oxide by ruthenium porphyrins

EXPERIMENTAL SECTION

General Methods.

Infrared (ir) spectra were recorded in a JASCO DS-701G spectrophotometer. Proton nuclear magnetic

resonance (^{1}H-nmr) spectra were recorded on a Hitachi R-24B (60MHz) or a JEOL JNM GSX-400 (400MHz) pulse Fourier-transform nmr spectrometer. Chemical shifts are expressed in units (ppm) downfield of internal tetramethylsilane. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are expressed in Hz. Ultraviolet and visible (uv) absorption spectra were recorded on a Hitachi 557 double-beam spectrophotometer equipped with thermostatic cell compartments.

Gas chromatography was done using a Shimadzu GC-6A, a Shimadzu GC-7A and a Shimadzu GC-14A, with flame ionization detector (FID) and a Shimadzu Chromatopac C-R5A. The columns employed were 10% PEG on Shimalite W mesh 60-80 (2.0 m x 2 6 mm i. d.), 3% OV-17 on Gaschrom Q mesh 100-120 (2.0 m x 2.6 mm i. d.) packed in a glass column, OV-101 fused silica capillary column (0.25 μm thickness, 20 m x 0.25 mm i. d.), Widebore column CBP20-WW12-100 (12 m x 0.53 mm) (Shimadzu) and Megabore column DB-5 (15 m) (J&W Company, Ltd.), with 40 ml/min of nitrogen as the carrier gas.

Gas chromatography/electron impact-mass spectral analysis was performed with a Shimadzu QP-2000A mass spectrometer (coupled with a Shimadzu GC-14A gas chromatograph). The column employed was the Megabore column DB-5 (15 m) (J&W Company, Ltd.) with 40 ml/min of nitrogen as the carrier gas.

Materials.

Commercial benzene and CH_2Cl_2 of reagent-grade quality were distilled from CaH_2 and stored over 4A molecular sieves. Benzene-d_6 was purchased from Aldrich Chemical Co., Inc and was used as received. Water-^{18}O ($H_2{}^{18}O$) (97.2 atom % ^{18}O) was purchased from MSD Isotopes (division of Merck Frosst Canada, Inc.) and was used as received. Hydrochloric acid (36%) and hydrobromic acid (47%) were commercial products and were used as received.

All the starting substrates and compounds used as references in product analyses were of the highest purity commercially available unless otherwise stated, and were used as received or were purified by distillation or recrystallization, if necessary. *cis*-1-Phenylpropene (*cis*-β-methylstyrene) (**15a**) was prepared by the reduction of 1-phenylacetylene with H_2.[51] Some of the epoxides and sulfoxides were prepared by the oxidation of corresponding substrates with mCPBA in CH_2Cl_2.

All the commercial samples of *N*-oxides were used after being purified by passage through aluminum oxide. 2,6-Dichloropyridine *N*-oxide (**3f**) and 2,6-dibromopyridine *N*-oxide (**3g**) were prepared by oxidation of the corresponding pyridines with CF_3COOOH[52] and were recrystallized from benzene and ethanol, respectively. 2,4,6-Collidine *N*-oxide (**3d**) was prepared by the oxidation of collidine with CH_3COOOH and was passed

through aluminum oxide. 2,6-Diphenylpyridine *N*-oxide (**3h**) was prepared by oxidation of the corresponding pyridine with mCPBA in CH_2Cl_2, and was recrystallized from benzene / n-hexane. 2,3,5,6-Tetramethylpyrazine *N*-oxide (**38**) and *N,N'*-dioxide (**37**) were prepared by the oxidation of 2,3,5,6-tetramethylpyrazine with mCPBA in CH_2Cl_2, and were recrystallized from n-hexane and benzene, respectively. 2-Methylquinoline (quinaldine) *N*-oxide (**46**) and acridine *N*-oxide (**48**) were also prepared by oxidation of the corresponding quinolines with mCPBA in CH_2Cl_2, and were purified by alumina column chromatography.

RuTMP(CO) (**1a**) and RuTMP$(O)_2$ (**1b**) were prepared according to Groves and Quinn.[34a] RuTPP(CO) (**2**) was a commercial sample from Aldrich Chemical Co., Inc. *Other porphyrin complexes*, FeTMPCl, MnTMPCl, MnTDFPPCl, CoTPP, MoTMP(O)(OH) and RhTMP(Cl), were synthesized according to the established methods.[53,54] $Ru(PPh_3)_4Cl_2$ and $Ru(PPh_3)_3Cl_2$ were prepared according to the literature.[55]

Epoxidation of Olefins and the Analysis of Products.

The epoxidation of styrene is described as a typical procedure. A solution of styrene (**5**) (104 mg, 1.0 mmol), dichloropyridine *N*-oxide (**3f**) (180 mg, 1.1 mmol) and RuTMP$(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred under argon at room temperature overnight. *p*-Dichlorobenzene was added to the reaction mixture as an internal standard and then gc analysis was performed with a 10% PEG column (2.0 m)

The epoxidation of norbornene was carried out as follows. To a solution of norbornene (94 mg, 1.0 mmol) and 2,6-dichloropyridine *N*-oxide (**3f**) (180 mg, 1.1 mmol) in benzene (5 ml) was added 1 ml of a benzene solution of RuTMP$(O)_2$ (**1b**) (30~36 μM). The mixture was stirred under argon at room temperature for 1 day. The internal standard was added, and the resulting mixture analyzed by gc with a 10% PEG column (2.0 m). The conditions and the retention times (min) were as follows. (i) Oxidation of styrene: at 150°C (injection temperature: 170°C), retention times (min): *p*-dichlorobenzene (internal standard), 3.40; styrene oxide (**6**), 6.48. (ii) Oxidation of norbornene: at 130°C (injection temeperature: 150°C), retention times (min): norbornene oxide, 3.07; *p*-dichlorobenzene (internal standard), 5.43.

Isolation of Several Epoxides.

p-Chlorostyrene oxide (**8**) was prepared by the typical procedure. A solution of *p*-chlorostyrene (**7**) (140 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (135 mg, 1.1 mmol) and RuTMP$(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred at room temperature under argon for 6 h. The reaction mixture was chromatographed on silica gel to afford *p*-chlorostyrene oxide (**8**) (154 mg, 99 %).

Competitive Epoxidations between *cis*- and *trans*-Olefins.

The competitive epoxidations between *cis*- and *trans*-stilbene were carried out as follows. A solution of *cis*-stilbene (**11a**) (180 mg, 1.0 mmol), *trans*-stilbene (**11b**) (180 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (123 mg, 1.0 mmol) and $RuTMP(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred at room temperature under argon overnight. The reaction mixture was washed with 10% citrate solution and brine to remove 2,6-lutidine (**4c**). The organic layer was evaporated and the residue was separated into epoxides and unreacted olefins by silica gel column chromatography (benzene). The mixture of *cis*- (**12a**) and *trans*-epoxides (**12b**) was analyzed by ^{1}H-nmr (400 MHz), and the *cis* / *trans* ratio was determined by comparing the relative integral intensities of oxiran proton of both epoxides [*cis* (**12a**): δ 4.36 (s, 2H); *trans* (**12b**): δ 3.83 (s, 2H)]. The mixture of unreacted *cis*- and *trans*-stilbenes was also analyzed and the *cis* / *trans* ratio was determined by comparing the relative integral intensities of olefinic proton signals [*cis* (**11a**): δ 6.62 (s, 2H); *trans* (**11b**): δ 7.11 (s, 2H)].

The competitive epoxidation of *cis*- (**15a**) and *trans*-β-methylstyrenes (**15b**) was carried out according to the procedure described above, but the analysis of the resulting mixture was performed by gas chromatography with a 10% PEG column (2.0m) (injection temperature: 190°C, column temperature: 170°C, internal standard: naphthalene).

The epoxidation of *trans,cis,trans*-1,5,9-cyclododecatriene (**17**) was carried out as follows. A solution of *trans,cis,trans*-1,5,9-cyclododecatriene (**17**) (162 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (123 mg, 1.0 mmol), and $RuTMP(O)_2$ (**1b**) (5.5 mg 6 μmol) in benzene (6 ml) was stirred under argon at room temperature overnight. The mixture of epoxides was separated from the resulting solution by silica gel column chromatography, and the yields of epoxides was determined. Then the mixture of epoxides was analyzed by ^{1}H-nmr (400 MHz), and the ratio of *cis*- (**18a**) and *trans*-epoxides (**18b**) was determined.[19a]

Epoxidations of Terpenes

A solution of geranyl acetate (**19a**) (196 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (160 mg, 1.3 mmol) and $RuTMP(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred under Ar at room temperature overnight. Ether (10 ml) was added and the mixture was washed with 10% aqueous citrate solution and then brine. The organic layer was dried over $NaSO_4$ and evaporated. The residue was separated into a mixture of epoxides (6,7-epoxide (**20a**), 2,3-epoxide (**21a**) and 2,3-6,7-diepoxide (**22a**)) and unreacted geranyl acetate The mixture of epoxides was analyzed by ^{1}H-nmr (400 MHz), and the ratio of the among three epoxidated compounds was determined by comparing the relative integral intensities of oxiran protons and olefin protons of these compounds.[27,56] The epoxidations of neryl acetate (**19b**) and linalyl acetate (**19c**) were carried out

according to the same procedure.

Oxidations of Allyl or Benzyl Alcohols

The oxidations of alcohols were carried out as follows. A solution of benzyl alcohol (**23**) (108 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (123 mg, 1.0 mmol), and $RuTMP(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred under Ar at room temperature overnight. *p*-Dichlorobenzene (internal standard) was added, and the yield of benzaldehyde (**24**) was determined by gc with a 10% PEG column (2.0 m). The reaction with 2-phenethyl alcohol (**29**) was also carried out in a similar manner. The retention times (min) were as follows: at 150°C (injection temperature 170°C), *p*-dichlorobenzene, 2.38; benzaldehyde (**24**), 3.21; 2-phenethylaldehyde (**30**), 5.09; 2-phenethyl alcohol (**29**), 14.1.

Some of the aldehydes were isolated according to the following procedure. A solution of cinnamyl alcohol (**25**) (134 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (123 mg, 1.0 mmol), and $RuTMP(O)_2$ (**1b**) (5.5 mg, 6 μmol) in benzene (6 ml) was stirred under Ar at room temperature overnight. The resulting mixture was chromatographed on silica gel (*n*-hexane : CH_2Cl_2 = 1 : 3) to afford cinnamaldehyde Isolated yields are given in the text.

Oxidations of Sulfides

A solution of phenyl methyl sulfide (thioanisole) (**31**) (124 mg, 1.0 mmol), 2,6-lutidine *N*-oxide (**3c**) (123 mg, 1 0 mmol) and $RuTMP(O)_2$ (**1b**) (9.1 mg, 10 μmol) in benzene (10 ml) was refluxed under Ar for 30 min. The resulting mixture was analyzed by gas chromatography with a 10% PEG column (2.0 m) at 195°C (injection temperature. 200°C) and the yields of sulfoxide (**32**) and sulfone (**33**) were determined. The retention times (min) were as follows: phenyl methyl sulfide (**31**), 1.44; 1-methylnaphthalene (internal standard), 3.61; phenylmethylsulfoxide (**32**), 9.85; phenylmethylsulfone (**33**), 20.3. The other reactions with phenylmethylsulfide (**31**) were carried out in a similar manner.

It took 2 h for the oxidation of benzyl sulfide (**34**) to go to completion under the conditions described above. Chromatographic separation of the resulting mixture on a column of silica gel (*n*-hexane : CH_2Cl_2 = 1 : 2) gave the mixture of sulfoxide (**35**) and sulfone (**36**), and the rate of sulfoxide / sulfone ratio was determined from the relative intensities of benzyl protons in the ^1H-nmr (400 MHz) spectrum [sulfoxide (**35**): δ 3.59 (s, 4H); sulfone (**36**): δ 4.13 (s, 4H)].

Epoxidations of Styrene with Various Heteroaromatic *N*-Oxides.

The epoxidations of styrene (**5**) with various heteroaromatic *N*-oxides were carried out as follows. To a solution of styrene (**5**) (1.0 mmol) and heteroaromatic *N*-oxide (1.1 mmol) in benzene (6 ml) was added

$RuTMP(O)_2$ (**1b**) (6 μmol). The mixture were stirred under Ar at room temperature for 1 day, and then *p*-dichlorobenzene was added as an internal standard. The reaction mixture was analyzed by gc with a 10% PEG (2 m) at 150°C (injection temperature: 170°C) or with an OV-101 fused silica capillary column (20 m) at 120°C (injection temperature: 130°C). The retention times (min) with the OV-101 column at 120°C were as follows: styrene (**5**), 4.82; *p*-dichlorobenzene (internal standard), 6.90; styrene oxide (**6**), 8.07; 2,3,5,6-tetramethylpyrazine (**39**), 8.82; 2-methylquinoline (quinaldine) (**47**), 23.2. The retention times (min) with a 10% PEG column at 150°C are given above.

Oxidations of Adamantane in the Presence of HCl or HBr.

A typical procedure for the oxidation of adamantane shown in Table IX is as follows. To a solution of adamantane (**50**) (136 mg, 1.0 mmol) and 2,6-dichloropyridine *N*-oxide (**3f**) (213 mg, 1.3 mmol) in benzene (5 ml) were added molecular sieves 4A (500 mg) and three or four drops of hydrobromic acid (47%). Next, RuTPP(CO) (**2**) (3.7 mg, 5.0 μmol) was added and the mixture was stirred at room temperature under argon Naphthalene (internal standard) was added 24 h after the start of the reaction, and the mixture was analyzed by gc. The temperature and the retention times for reagents and products are given below With an OV-17 column (2.0 m), the retention times (min) were as follows: at 120°C (injection temperature 150°C), adamantane (**50**), 1.43; 2,6-dichloropyridine (**4f**), 2.50; naphthalene (internal standard), 3.51; adamantan-1-ol (**51**), 4.92; adamantan-2-ol (**53**), 7.01; adamantan-2-one (**54**), 8 50; adamantane-1,3-diol (**52**), 17.8.

A typical procedure for the oxidations of adamantane (**50**) with 10^{-4} ~ 10^{-5} eq. of the catalyst was as follows. To a solution of adamantane (**50**) (680mg, 5.0 mmol) and 2,6-dichloropyridine *N*-oxide (**3f**) (1.06g, 5.0 mmol) in benzene (2.5 ml) were added molecular sieves 4A (500 mg) and three or four drops of hydrobromic acid (47%). Next, a 0.02 mM solution of RuTPP(CO) (**2**) (0.05 μmol) in benzene (2.5 ml) was added, and the mixture was stirred at 40°C under argon. Naphthalene (internal standard) was added to the mixture 6 days after the start of the reaction, and the yields of the oxidized products were determined by gc under the conditions described above.

Oxidations of Alkanes or Aliphatic alcohols in the Presence of HCl or HBr

The oxidation of methylcyclohexane (**55**) and the analysis of the resulting products were carried out as follows. To a solution of methylcyclohexane (**55**) (98 mg, 1.0 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (328 mg, 2.0 mmol), and RuTPP(CO) (**2**) (3.7 mg, 5 μmol) in benzene (5 ml) were added molecular sieves 4A (500 mg) and 3~4 drops of hydrobromic acid (47%). The mixture was stirred under Ar at room temperature for 6 h and then naphthalene was added as an internal standard. Gc Analysis was performed by

withdrawing several aliquots with the aid of a micro-syringe, and the yield of 1-methylcyclohexanol (**56**) was determined. The conditions and the retention times (min) were as follows: OV-101 fused silica capillary column (20 m), at 100°C (injection temparature 150°C); *retention times (min)*: 1-*methylcyclohexanol* (**56**), 6.68; naphthalene (internal standard), 25.7. After the initial analysis, a solution of *O*-methylhydroxylamine HCl (2% w/v in pyridine, 2 ml) was added to the reaction mixture. The mixture was heated at 75°C for 1 h and *p*-dichlorobenzene was added as another internal standard. The gc analysis with the same column was carried out again under the following conditions. At 70°C (injection temperature: 150°C); retention times (min): *p*-dichlorobenzene (internal standard), 28.5; 2-methylcyclohexane-O-methoxime, 36.9 and 37.4 (*cis* and *trans*); 3-methylcyclohexane-*O*-methoxime, 37.3 and 38.4 (*cis* and *trans*); 4-methylcyclohexane-O-methoxime, 39.5. The yields of methylcyclohexanones (**58**) were determined by comparing the areas of these peaks The oxidation of methylcyclohexane (**55**) with RuTMP(O)$_2$ (**1b**) was carried out at 40°C according to the same procedure.

The oxidation of *cis*-decalin (**59a**) and the isolation of the resulting *cis*-9-decalol (**60a**) was carried out as follows. To a solution of *cis*-decalin (**59a**) (138 mg, 1.0 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (196 mg, 1.2 mmol), and RuTPP(CO) (**2**) (3.7 mg, 5 μmol) in benzene (5 ml) were added molecular sieves 4A (500mg) and 3~4 drops of hydrobromic acid (47%). The mixture was stirred under Ar at room temperature for 6 h and then chromatographed on silica gel to afford *cis*-9-decalol (**60a**).[57] The oxidation of adamantan-1-ol (**51**) and the isolation of the resulting adamantane-1,3-diol (**52**)[57] were performed at 65°C in almost the same manner.

The oxidations of secondary alkanes were carried out as follows. To a solution of cyclooctane (**64**) (56 mg, 0.50 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (246 mg, 1 50 mmol), and RuTPP(CO) (**2**) (1.8 mg, 2.5 μmol) in benzene (2.5 ml) were added molecular sieves 4A (250mg) and 2 drops of hydrobromic acid (47%). The mixture was stirred under Ar at room temperature for 40 h and then *p*-dichlorobenzene was added as an internal standard. The mixture was analyzed by gc and the yields of cyclooctanol (**65**) and cyclooctanone (**66**) were determined The oxidation of ethylbenzene (**61**) was carried out with RuTMP(O)$_2$ (**1b**) as the catalyst. The conditions and the retention times (min) for the substrates and products are given below. With a OV-101 fused silica capillary column (20 m), at 150°C (injection temparature 180°C), the retention times (min) were as follows: cyclooctane (**64**), 3 35; *p*-dichlorobenzene (internal standard), 3.83; cyclooctanone (**66**), 4.83; cyclooctanol (**65**), 5.16. With a 10% PEG column (2.0m), at 170°C (injection temparature 190°C), the retention times (min) were as follows: ethylbenzene (**61**), 0 79; *p*-dichlorobenzene (internal standard), 2.24; acetophenone (**63**), 4 81; 1-phenethyl alcohol (**62**), 8.50.

The oxidation of cyclohexanol was carried out as follows. To a solution of cyclohexanol (**67**) (100 mg, 1.0 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (196 mg, 1.2 mmol), and RuTMP(O)$_2$ (**1b**) (4.5 mg, 5 μmol) in benzene (5 ml) was added molecular sieves 4A (500 mg) and 3~4 drops of hydrochloric acid (36%). The mixture was stirred under Ar at room temperature for 1 day and the yields of products were determined by gc according to the following conditions: Column, 10% PEG (2.0 m); injection temparature, 150°C; column temperature, 120°C; retention time (min), cyclohexanone (**68**), 2.80, cyclohexanol (**67**), 4.04, *p*-dichlorobenezene (internal standard), 5.30.

Competitive Hydroxylation between *cis*- and *trans*-Decalins

To a solution of *cis*-decalin (**59a**) (138 mg, 1.0 mmol), *trans*-decalin (**59b**) (138 mg, 1.0 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (213 mg, 1.3 mmol), and RuTPP(CO) (**2**) (3.7 mg, 5 μmol) in benzene (5 ml) were added molecular sieves 4A (500 mg) and 3~4 drops of hydrobromic acid (47%). The mixture was stirred under Ar at room temperature for 12 h and then naphthalene was added as an internal standard. The analysis of the mixture was performed by gc with an OV-101 fused silica capillary column (20m) at 150°C (injection temperature, 180°C) and the yields of alcohols were determined. The retention times (min) were follows: *trans*-decalin (**59b**), 5.15; 2,6-dichloropyridine (**4f**), 5.18; *cis*-decalin (**59a**), 5.71; naphthalene (internal standard), 6.85; *trans*-decalol (**60b**), 7.93; *cis*-decalol (**60a**), 8.77. Next, *p*-dichlorobenzene was added and the mixture was analyzed again by gc with a Widebore column CBP20-WW12-100 (12m) at 80°C (injection temperature 120°C), to determine the recoveries of decalins. The retention times (min) were follows: *trans*-decalin (**59b**), 1.12; *cis*-decalin (**59a**), 1.51; *p*-dichlorobenzene (internal standard), 4.53

Reaction of RuTMP(O)$_2$ with Vinylnaphthalene

The reaction of RuTMP(O)$_2$ (**1b**) with vinylnaphthalene (**69**) was carried out in an nmr tube at 30°C as follows. A solution of vinylnaphthalene (**69**) (12 mg, 0.08 mmol) and toluene (internal standard) in benzene-d_6 (0.6 ml) was placed in an nmr tube. The solution was bubbled with argon and the tube was capped. Into the tube was injected 0.2 ml of a 4mM solution of RuTMP(O)$_2$ (**1b**) (0.8 μmol) in benzene-d_6 which had also been bubbled with argon. The 400 MHz ^{1}H-nmr spectrum of this solution was measured at intervals, and the concentration of RuTMP(O)$_2$ (**1b**) at each time were determined by comparing the relative proton integral intensities of the pyrrolic protons of RuTMP(O)$_2$ (**1b**) (δ 9.02, s, 8H) and the methyl protons of toluene (δ 2.11, s, 3H).

The catalytic epoxidation of vinylnaphthalene with 2,6-lutidine *N*-oxide (**3c**) in the presence of RuTMP(O)$_2$ (**1b**) was also carried out in an nmr tube at 30°C. A solution of vinylnaphthalene (12 mg, 0.08 mmol), 2,6-

lutidine *N*-oxide (**3c**) (9.8 mg, 0 08 mmol) and toluene (internal standard) in benzene-d_6 (0 6 ml) was placed in an nmr tube. The solution was bubbled with argon and the tube was capped. Into the tube was injected 0.2 ml of a solution of RuTMP(O)$_2$ (**1b**) (4 mM) in benzene-d_6 which had also been bubbled with argon. The 400 MHz ^{1}H-nmr spectrum of this solution was measured at intervals, and the concentration of vinylnaphthalene (**69**) at each time was determined by comparing the relative proton integral intensities of the olefinic protons of vinylnaphthalene (**69**) (δ 5.17, dd , 1H, J=11 2, 0.8; δ 5.71, dd , 1H, J=17.6, 0.8; δ 6.74, dd , 1H, J=17.6, 11.2) and the methyl protons of toluene.

Epoxidation of Styrene in the Presence of $H_2{}^{18}O$

Epoxidation of styrene (**5**) in the presence of $H_2{}^{18}O$ was carried out as follows To a solution of styrene (**5**) (10 mg, 0.1 mmol), 2,6-lutidine *N*-oxide (**3c**) (12 mg, 0.1 mmol), and RuTMP(O)$_2$ (**1b**) (1.8 mg, 2 μmol) in benzene (2 ml) was added 20 μl of $H_2{}^{18}O$, and the mixture was stirred under Ar at room temperature for 1 day. The resulting solution was analyzed by gc/ms. The mass pattern of the peak of styrene oxide (**6**) was recorded. The ratio of styrene oxide-^{18}O / styrene oxide-^{16}O was determined by comparing the relative peak intensities of the peak 122 (m/z, M$^+$ for styrene oxide-^{18}O) and the peak 120 (m/z, M$^+$ for styrene oxide-^{16}O). The analytical gc employed a Megabore column DB-5 (15 m) under following conditions: injection temperature, 170°C; temperature program, 60-200°C (initial time: 3 min, final time: 5 min, rate: 10°C/min). The retention times (min) were as follows: styrene oxide (**6**), 7.45; phenylacetaldehyde, 7.20. After the gc/ms analysis, *p*-dichlorobenzene was added to the resulting mixture as an internal standard. The solution was also analyzed by gc with an OV-101 fused silica capillary column (20 m) at 130°C (injection temperature 120°C) and the yield of styrene was determined. The retention times (min) were as follows: styrene oxide (**6**), 8.16; phenylacetaldehyde, 7.34. The epoxidation of styrene was also carried out in the absence of 2,6-lutidine *N*-oxide (**3c**) under O_2 according to the procedure described above.

The Reaction of RuTMP(O)$_2$ with HCl

To a solution of RuTMP(O)$_2$ (**1b**) (18 mg, 0.02 mmol) in benzene (20 ml) were added molecular sieves 4A (2 g) and hydrochloric acid (36%) (0.8 ml). The mixture was stirred under Ar at room temperature for 4 h. The resulting mixture was filtered and the filtrate was evaporated. The ^{1}H-nmr (400 MHz) spectrum of the resulting crystals was measured in $CDCl_3$ [δ −54.65 (pyrrolic proton) (bs, 8H), 3.84 (*para*-methyl proton) (s, 12H), 4.07 (*ortho*-methyl proton) (s, 24H), 12.49 (*meta*-proton) (s, 8H)]. Uv/vis (benzene, 25°C; λ_{max}, nm(ε)): 552(sh), 515(5750), 407(141000).

Catalytic Oxidation of Adamantane with RuTMP Complexes

These catalytic reactions were carried out as follows. A solution of adamantane (**50**) (27.2 mg, 0.20 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (32.8 mg, 0 20 mmol) and RuTMP(O)$_2$ (**1b**) (0.7 mg , 0.8 μmol) in benzene (2 ml) was stirred under Ar at 40°C. The reaction mixture was analyzed by gc with OV-17 (2.0 m) at 140°C (injection temperature: 170°C). The retention times were as follows: adamantan-1-ol (**51**), 2.48; adamantane-1,3-diol (**52**), 7.71; diphenyl (internal standard), 4.84.

Catalytic Oxidation of Adamantane with RuTMP(O)$_2$ in the Presence of Dry HCl

These catalytic reactions were carried out as follows. To a solution of adamantane (**50**) (27.2 mg, 0.20 mmol), 2,6-dichloropyridine *N*-oxide (**3f**) (32.8 mg, 0.20 mmol) and RuTMP(O)$_2$ (**1b**) (0.7 mg, 0.8 μmol) in benzene (2 ml) was added a saturated HCl solution of benzene (10 ml/l, 5 ml/l, or 0 ml/l). The mixture was stirred under Ar at 40°C, and analyzed by gc under the conditions described above.

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

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30. We found that the addition of various metal salts or complexes, such as $Ni(PPh_3)_2Cl_2$, $NiCl_2$, $NiBr_2$, $CoCl_2$ and interestingly $Ru(PPh_3)_4Cl_2$, enhances the epoxidation of olefins or other oxidations with ruthenium porphyrin and lutidine *N*-oxide. For example, cyclohexanol (20 mg, 0 20 mmol) was oxidized with $RuTMP(O)_2$ (3.6 mg, 4 μmol) and lutidine *N*-oxide (24.6 mg, 0.22 mmol) at room temperature in 4 days to afford cyclohexanone in 8% yield based on cyclohexanol On the contrary, the oxidation of cyclohexanol under the same conditions except that the reaction mixture contained $Ni(PPh_3)_2Cl_2$ (3.6 mg, 4 μmol) as an additive, proceeded efficiently, and cyclohexanone was obtained in 95% yield. The metal salts or complexes may play two roles for the enhancement of these reactions, similarly to HCl or HBr. The first is to convert the dioxo complexes of ruthenium porphyrins into appropriate complexes, and the second is to accelerate the deoxygenation of *N*-oxide by ruthenium porphyrins owing to their Lewis acidity.

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43. It was indicated that the oxidation reactivities of the oxo-metal species of some porphyrin or salen complexes were activated by the coordination of such *N*-oxides as σ-donor ligands.[19e,4k] Thus, the 4-valent Ru porphyrin mono oxo complex coordinated by substituted pyridine *N*-oxide as an axial ligand is also a candidate for the intermediate. The 4-valent Ru-oxo species are believed to be active intermediates even for catalytic alkane oxidations.[44]
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Received, 21st July, 1994