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HIGHLY EFFICIENT OXYGEN TRANSFER REACTIONS FROM VARIOUS HETEROAROMATIC N-OXIDES TO OLEFINS, ALCOHOLS, AND SULFIDES CATALYZED BY RUTHENIUM PORPHYRIN

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SUMMARY Ruthenium porphyrin catalyzed the oxygen transfer reactions from various heteroaromatic N-oxides to olefins, alcohols, and sulfides to afford epoxides, aldehydes, and sulfoxides, respectively, in satisfactory yield.

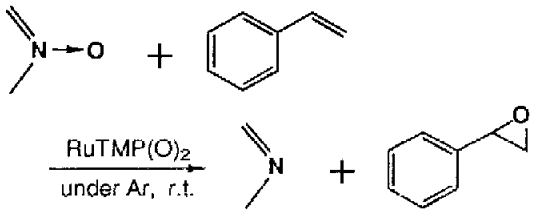
Much interest has been focused on the reactivity of metalloporphyrin complexes, not only because of the relation of these reactions to that of cytochrome P-450 or other heme containing enzymes, but also because of the high potential of these complexes as oxidation / reduction catalysts[1].

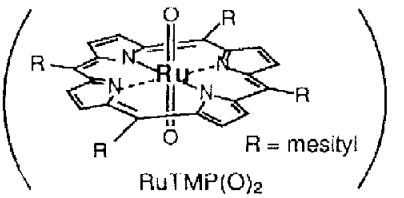
We recently described the unique reactivity of ruthenium porphyrin complexes to catalyze the oxygen atom transfer reactions from pyridine N-oxides to olefins which had not been reported to proceed catalytically[2]. In this system, olefins were converted into their epoxides selectively with high efficiency under mild conditions. In this report further extension of the scope of this system is described.

We first wish to report the ability of other heteroaromatic N-oxides, which are as stable as pyridine N-oxides[3], as the oxidants for this system. A variety of heteroaromatic N-oxides (180 mM) were allowed to react with styrene (170 mM) in the presence of catalytic amounts of $RuTMP(O)_2$ [dioxo(tetramesitylporphyrinato)ruthenium(VI)][4] (1 mM) as summarized in Table 1. It was proved that the N-oxides of 2,3,5,6-tetra-methylpyrazine, acridine, 2-methylquinoline, and 3,6-dichloropyridazine react as the oxidants of this catalytic reaction (entry 1~5), but not 4,6-

dimethyltriazine N-oxide (entry 6). 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 other heteroaromatic N-oxides could act as novel 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[5]. Interestingly, 2,6-diphenylpyridine N-oxide could not be an effective oxidant for this system (entry 7). Too large substituents may interfere with the interaction even between the oxygen atom of N-oxides and the metal.

Substrates other than olefins were oxidized with this system. The results for the oxidation of alcohols[6] are summarized in Table 2. Allyl alcohols (170 mM) were oxidized with $RuTMP(O)_2$ (1 mM) / lutidine N-oxide (170 mM) to afford α,β-unsaturated aldehydes selectively





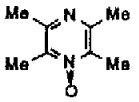
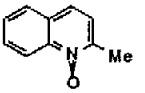
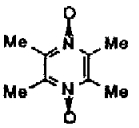
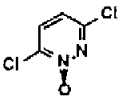
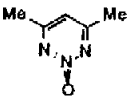
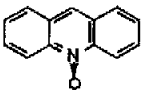
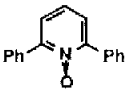
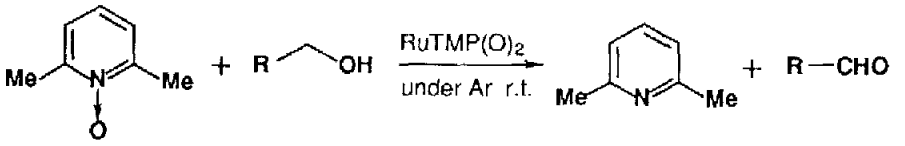
Entry	Oxidants	Yield[b] styrene oxide[c]	reduced oxidant[d]	Entry	Oxidants	Yield styrene oxide	reduced oxidant
1		100 %	100 %	4		46 %	42 %
2[a]		99 %	100 %	5		28 %	n.d.
				6		trace	n.d.
3		59 %	n.d.[e]	7		trace	n.d.

Table 1 These reactions were carried out in benzene at r.t. under Ar for 1day ([styrene]=170mM, [N-oxide]=180mM, [$RuTMP(O)_2$]=1mM). a) [N-oxide]=90mM. b) Detected by G.L.C. c) Based on styrene. d) Based on N-oxide. e) Not determined.

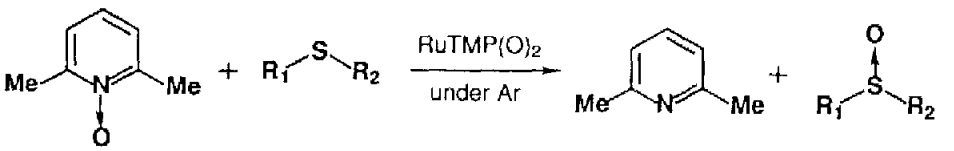
(entry 1 and 2)[7]. The reaction of benzyl alcohol also proceeded efficiently (entry 3) but not that of 2-phenylethanol (entry 4).

Table 3 shows the results for the oxidation of sulfides under a variety of conditions. The oxygen transfer reaction from lutidine N-oxide (200 mM) to phenyl methyl sulfide (200 mM) in the presence of $RuTMP(O)_2$ (2 mM) did not proceed as efficiently as the oxidation of olefins or alcohols requiring 6 days for the complete consumption of sulfide at room temperature (entry 2). However, in refluxing benzene sulfide was exhausted during half an hour to afford sulfoxide mainly (entry 1). Heating the solution (80°) forced the reaction catalyzed by $Ru(PPh_3)_4Cl_2$ to proceed as well, but it took 4 hr for completion (entry 3). The rate of oxidation of benzyl sulfide



Entry	Alcohols	Yield (Aldehyde)	
1	3-phenyl-2-propenol	79%[a,c]	(87%)[b]
2	geraniol	45%[c]	(65%)
3	benzyl alcohol	81%[d]	
4	2-phenylethanol	2%[d]	

Table 2 These reactions were carried out in benzene at r.t. under Ar overnight ([alcohol]=170mM, [lutidine N-oxide]=170mM, [$RuTMP(O)_2$] =1mM). a) Based on alcohols. b) Based on conversion. c) Isolated yield. d) Determined by G.L.C.



Entry	Sulfides	Catalysts	Conditions		Yield[a] Sulfoxide	Sulfone
1	phenyl methyl sulfide	$RuTMP(O)_2$	reflux	0.5h	90%[b]	7%[b]
2		$RuTMP(O)_2$	r.t.	6d	85%	2%
3		$Ru(PPh_3)_4Cl_2$	reflux	4h	80%	4%
4		none	reflux	10h	4%	2%
5	benzyl sulfide	$RuTMP(O)_2$	reflux	2h	94%[c]	3%[c]

Table 3 These reactions were carried out in benzene under Ar ([sulfide]=200mM, [lutidine N-oxide]=200mM, [catalyst]=2mM). a) Based on sulfide. b) Determined by G.L.C. c) Isolated yield.

was slower than that of phenyl methyl sulfide under the same condition (entry 5). The competitive reaction of benzyl sulfide and phenyl methyl sulfide was examined to give the results that the reaction proceeded as slowly as did the oxidation of benzyl sulfide alone and that benzyl sulfide was rather reactive than phenyl methyl sulfide (the ratio of resulting sulfoxides : benzyl sulfoxide / phenyl methyl sulfoxide = 6 / 4). An explanation that sulfides or the resulting sulfoxides coordinate with porphyrin metal to inhibit the catalytic reaction competitively and benzyl sulfide or its sulfoxide can coordinate more strongly than phenyl methyl sulfide or its sulfoxide is plausible for these reactivities of sulfides.

More applications of this system have been investigated in our laboratory and the mechanistic details will be discussed elsewhere.

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References and Notes

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4) Groves, J. T. , Quinn, R., *Inorg. Chem.*, **1984**, *23*, 2844.

5) We previously reported that substituents at the 2 and 6 positions on the pyridine rings were necessary for pyridine N-oxide derivatives to react as effective oxidants for this system, which was explained in the same way.

6) The oxygen transfer reaction from pyridine N-oxide to alcohols was previously tried with ruthenium catalysts, however, it failed (Sharpless, K. B., Akashi, K., Oshima, K., *Tetrahedron Lett.*, **1976**, 2503).

7) Geranyl acetate was oxidized with this system to afford 6,7-epoxide mainly.

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