Nitrous Oxide Oxidation of Olefins Catalyzed by Ruthenium Porphyrin Complexes

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In the presence of a catalytic amount of dioxo(tetramesitylporphyrinato)ruthenium(VI) complex, nitrous oxide (N_2O) oxidized trisubstituted olefins into the corresponding epoxides in good-to-high yields with high selectivities.

Nitrous oxide (N_2O) is one of the most popular nitrogen oxides.[1] It has been medically employed as an anesthetic gas, while a vast amount of nitrous oxide is emitted as a byproduct from the industrial manufacturing of nylon[2] and it has been recently implicated with global warming as a greenhouse gas.[3] In the field of synthetic organic chemistry, only several trials involving nitrous oxide were reported as practical reactions.[4] Since the decomposition of nitrous oxide into dinitrogen and oxygen atoms requires a high activation energy, nitrous oxide oxidation was usually performed under extremely drastic conditions, i.e., high temperature[4] and/or high pressure.[5] Nitrous oxide oxidation under mild conditions should provide a clean oxidation reaction because dinitrogen is the only waste. Hence, we attempted to employ transition-metal complexes as catalysts in order to lower the activation energy for the decomposition of nitrous oxide. The expected catalytic cycle is depicted as Figure 1; that is, a transition-metal complex receives an oxygen atom from nitrous oxide while releasing dinitrogen to generate the metal oxo complex, which oxidizes a substrate to regenerate the metal complex. Based on this working hypothesis, it was already found and reported that low-valent nickel complexes effectively activated nitrous oxide to oxidize phosphine(III) to phosphine oxide(V),[6] although this system was limited within the oxidation of phosphine derivatives. In this communication, we would like to describe the first success for catalytic nitrous oxide epoxidation of olefins using ruthenium porphyrin complexes as catalysts.

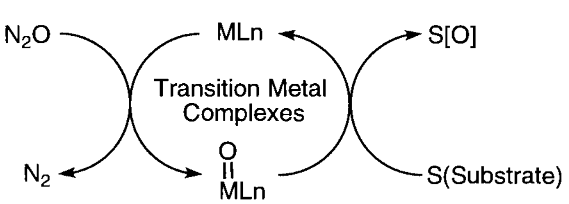
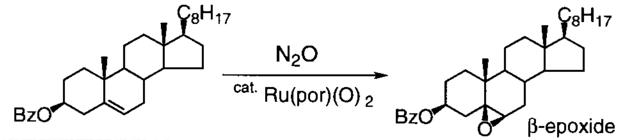


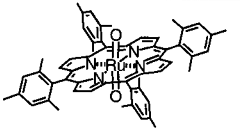
Figure 1. Catalytic cycle of N_2O oxidation.

It was reported that cholesteryl esters were preferentially epoxidized on their α-face using peroxy acid as an oxidant, while their β-epoxides were selectively obtained when transition-metal oxo species were used as oxidants.[7] Hence, cholesteryl esters were adopted as the probe for the transition-metal catalyzed nitrous oxide oxidation. After various transition-metal complexes were examined as catalysts for the nitrous oxide oxidation of cholesteryl benzoate, a β-selective epoxidized product was obtained in low yield using dioxo(tetramesitylporphyrinato)ruthenium(VI) ($Ru(TMP)(O)_2$) as a catalyst.

Table 1. N_2O oxidation of cholesteryl benzoate



Entry[a]	Solvent	Concentration /mM	Yield /%[e]	β-Selectivity /%
1	THF	33	0	-
2	EtOH	33	0	-
3	CH_3CN	33	0	-
4	Toluene	33	30	>99
5	Benzene	33	60	>99
6	Fluorobenzene	33	61	>99
7	Fluorobenzene	14[b]	99	>99
8[c]	Chlorobenzene	14[b]	94	>99
9[d]	Fluorobenzene	14[b]	78	>99



$Ru(TMP)(O)_2$

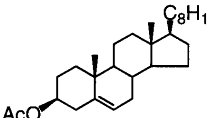
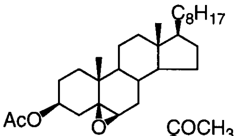
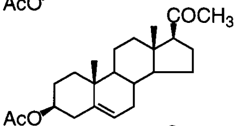
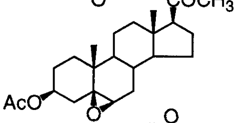
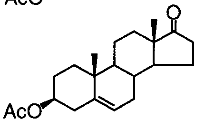
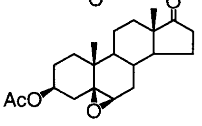
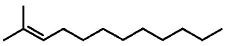
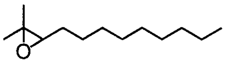
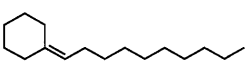
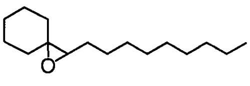
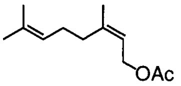
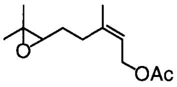
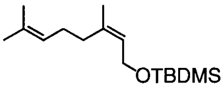
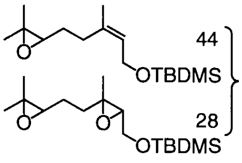
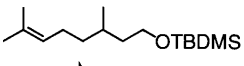
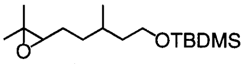
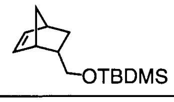
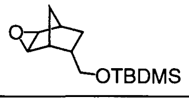
[a]Reaction conditions; 0.10 mmol cholesteryl benzoate and 5.0 mol% $Ru(TMP)(O)_2$ in solvent (3.0 mL) at 100 °C under 10 atm N_2O. [b]Reaction conditions; 0.20 mmol cholesteryl benzoate in 14 mL solvent. [c]Reaction was performed at 140 °C. [d]Dioxo[tetrakis(2,6-dichlorophenyl)porphyrinato]-ruthenium(VI) complex was used as a catalyst. [e]Isolated yield.

The transfer of an oxygen atom from nitrous oxide to Ru(TMP) and stoichiometric epoxidation of β-methylstyrene by the generated dioxoruthenium complex has already been reported by Groves et al.,[8] however, catalytic nitrous oxide epoxidation has not yet been reported, in spite of the fact that the possibility of a catalytic cycle was recognized.[9] This preliminary observation prompted us to examine the nitrous oxide oxidation of cholesteryl benzoate in the presence of a 5 mol% $Ru(TMP)(O)_2$ complex (Table 1).

When polar solvents, such as THF, EtOH, and acetonitrile, were used, no product was obtained (Entries 1–3). On the contrary, the nitrous oxide oxidation in toluene afforded the corresponding epoxide in moderate yield. A variety of aromatic solvents were examined and fluorobenzene was then found to be a suitable solvent (Entries 4–6).[10] Also, the concentration of the reaction was crucial; When the reaction was performed under diluted conditions, the yield of the epoxide attained 99% (Entry 7). It is assumed that the more nitrous oxide dissolved in the solution accelerated the reproduction of the dioxoruthenium complex in the catalytic cycle. Chlorobenzene was also a suitable solvent at 140 °C (Entry 8). Control experiments revealed that no reaction proceeded without the complex catalyst. Although a 9% yield of the product was obtained when the reaction was performed under an argon atmosphere in the presence of 5 mol% dioxoruthenium complex, it was considered that the oxygen atom of the epoxide was stoichiometrically transferred from the starting dioxoruthenium complex. When employing the dioxo(tetraphenylporphyrinato)ruthenium(VI), dioxo(octaethylporphyrinato)ruthenium(VI), and dioxo-[tetrakis(4-methoxyphenyl)porphyrinato]ruthenium(VI) complexes as catalysts, no product was obtained with almost total recovery of the cholesteryl benzoate. When the dioxo[tetrakis(2,6-dichlorophenyl)porphyrinato]ruthenium(VI) complex was used as a catalyst, the reaction proceeded to obtain the epoxidized product in 78% yield (Entry 9). These observations suggested that porphyrin complexes with sterically hindered aryl groups were effective catalysts for the nitrous oxide oxidation.[9,11] In all cases mentioned above, β-epoxides were predominantly obtained, and these selectivities indicated that the dioxoruthenium complexes reacted with the carbon–carbon double bonds in the cholesteryl benzoate during the oxidation step. This reaction would be the first success for transition-metal catalyzed epoxidation using nitrous oxide as an oxidant.

The catalytic nitrous oxide oxidation by ruthenium complexes was successfully applied to various olefinic compounds (Table 2).[12,13]

Table 2. N_2O oxidation of various olefinic compounds

Entry[a]	Substrates	Products	Yield /%
1			99
2			99
3			97
4[b] 5[c] 6 7[d]			48 63 76 86
8[d]			90
9[d]			64
10[d]			44 28 72 (total)
11[d]			94
12[d]			94

[a]Reaction conditions; 0.2 mmol olefins and 5.0 mol% Ru(TMP)(O)$_2$ in 14 mL chlorobenzene at 140 °C under 10 atm N_2O. [b]In 14 mL fluorobenzene at 100 °C. [c]In 14 mL fluorobenzene at 140 °C. [d]8.5 mol% catalyst was employed.

Cholesteryl acetate was epoxidized in quantitative yield (Entry 1), and other substrates with a steroidal framework were also oxidized in 97–99% yield (Entries 2 and 3). Various trisubstituted acyclic olefins were smoothly epoxidized with good-to-high yield. The isolated carbon-carbon double bond in neryl acetate was predominantly oxidized to afford the corresponding mono-epoxide in good yield (Entry 9). Although diepoxidation was observed during the epoxidation of *tert*-butyldimethylsilyl(TBDMS)ether of nerol, the isolated carbon-carbon double bond was preferentially oxidized compared with that of the allylic alcohol (Entry 10). Epoxidation of the TBDMS ether of citronellol proceeded to afford the corresponding epoxide in high yield (Entry 11). An activated disubstituted olefin could be easily epoxidized to afford the corresponding product in high yield (Entry 12).

In conclusion, the catalytic version of nitrous oxide epoxidation was achieved for the first time using 5 mol% Ru(TMP)(O)$_2$ as a catalyst to obtain the epoxides in good-to-high yield. A mechanistic study, the scope, and the limitations of the present oxidation system are currently in progress.

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10 The reactions in fluorobenzene also gave slightly better yields than in benzene for the other substrates.
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12 The nitrous oxide oxidation of olefins less reactive than cholesteryl benzoate, such as 2-methyl-2-dodecene and the TBDMS ether of nerol, did not complete at 100 °C in fluorobenzene, but better yields were obtained at 140 °C. Chlorobenzene was the suitable solvent compared with fluorobenzene for the reaction at 140 °C.
13 Typical procedure is as follows: To a chlorobenzene solution of Ru(TMP)(O)$_2$ (21 mg, 0.023 mmol) in an autoclave, 2-methyl-2-dodecene (50 mg, 0.27 mmol) was added under a nitrous oxide atmosphere. After the solvent amount was fixed at 14 mL, the reaction mixture was heated at 140 °C under 10 atm of N_2O for 5 h. The desired epoxide was purified through by silicagel column chromatography (Hexane:EtOAc 20:1, 86% yield).