

Nitrous Oxide Oxidation of Secondary and Benzylic Alcohols Using Ruthenium Complex Catalyst

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Catalytic N_2O oxidation of various secondary and benzylic alcohols using a ruthenium porphyrin complex is presented. Both secondary and benzylic alcohols were smoothly consumed to give the corresponding ketones and aldehydes in high yields. Nitrous oxide (N_2O) is expected to be a new terminal oxidant producing only dinitrogen gas as the only by-product to provide a less wasteful process.

Nitrous oxide (N_2O)¹ is emitted as a microbial product from the soil, while the industrial source resulting from manufacturing of 6,6-nylon increases its concentration in the atmosphere.² Because nitrous oxide causes a global warming effect³ as much as CO_2 , various methods for decomposing the waste nitrous oxide have been proposed.⁴ However, the alternative solution of utilizing nitrous oxide in synthetic organic chemistry as an oxidant has not been thoroughly investigated.⁵ Recently, we attempted to employ a transition metal complex as a catalyst to activate nitrous oxide and to utilize it as an oxidant. For example, utilizing a low valent nickel complex, catalytic oxidation of triarylphosphines to the corresponding phosphine oxides was carried out under atmospheric pressure with nitrous oxide.⁶ Also an effective epoxidation of olefins employing a catalytic amount of a dioxoruthenium porphyrin complex was realized (Figure 1, upper).⁷ The reaction was conducted under 10 atm of nitrous oxide in an autoclave, and excess nitrous oxide accelerated the regeneration of dioxoruthenium complex to oxidize olefins to epoxides effectively.

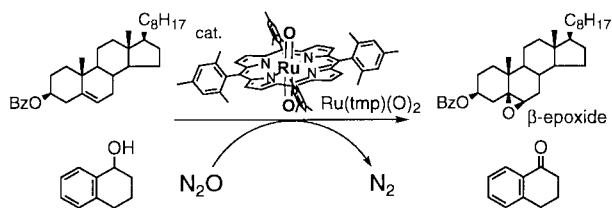


Figure 1. Catalytic N_2O oxidation of alkenes and *sec*-alcohols.

The oxidation of alcohols to the corresponding ketones and aldehydes is one of the most basic and important reactions in synthetic organic chemistry. Although many reagents have been developed to accomplish this fundamental reaction, some required highly toxic reagents and others excess reagent loading to the substrates. From an environmental and economical standpoint, a catalytic oxidation process⁸ could be extremely attractive. In this communication, we would like to describe that secondary and benzylic alcohols were effectively oxidized to the corresponding ketones and aldehydes with nitrous oxide in the presence of a catalytic amount of a ruthenium porphyrin⁹ complex (Figure 1, lower).

First the reaction conditions were examined in detail using

the oxidation of 2-naphthylmethanol as a model reaction (Table 1). Because aromatic solvents were preferred for the N_2O epoxidation catalyzed by a dioxoruthenium complex, the oxidation of alcohols was first examined under similar reaction conditions in various aromatic solvents. When benzene, fluorobenzene, and chlorobenzene were used as the reaction solvent, 2-naphthylmethanol was converted to 2-naphthaldehyde in moderate yield (Entries 1–3). Although the oxidation of alcohol hardly proceeded in halogenic solvents such as dichloromethane or chloroform (Entries 4 and 5), 1,2-dichloroethane¹⁰ was found to be a suitable solvent for this reaction system to give the corresponding aldehyde in good yield (Entry 6). The optimization of the reaction conditions revealed that 2-naphthylmethanol was quantitatively converted to 2-naphthaldehyde under 10 atm of nitrous oxide and at 120 °C for 9 h.

Table 1. N_2O oxidation of 2-naphthylmethanol

Entry ^a	Solvents	Temp. / °C	Conv. / % ^b	Yield / % ^b
1	PhH	100	41	41
2	PhF	100	62	62
3	PhCl	100	41	39
4	CH_2Cl_2	100	23	22
5	$CHCl_3$	100	33	32
6	$Cl-CH_2-CH_2-Cl$	100	71	71
7		120	100	quant ^c

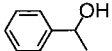
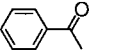
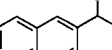
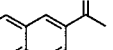
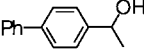
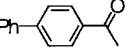
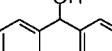
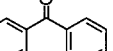
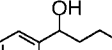
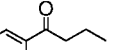
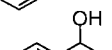
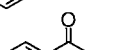
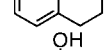
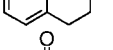
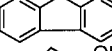
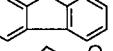
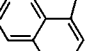
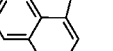
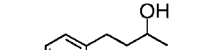
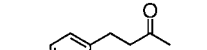

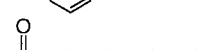
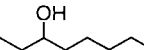
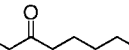
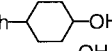
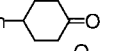


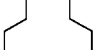
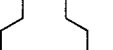
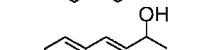
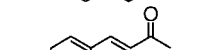
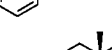

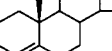
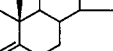
^aReaction conditions; 0.30 mmol of 2-naphthylmethanol and 5.0 mol% of $Ru(tmp)(O)_2$ in solvent (14.0 mL) under 10 atm of N_2O for 6 h.

^bIsolated yield. ^cAt 120 °C for 9 h.

The N_2O oxidation catalyzed by a ruthenium complex was successfully applied to various alcohols.¹¹ As well as 2-naphthylmethanol, 1-phenylethanol was selectively oxidized to acetophenone in 92% yield (Entry 1). Under the standard reaction conditions, various 1-arylethanol were smoothly consumed with high reactivity to give the corresponding aryl methyl ketones in excellent yields (Entries 2 and 3). High reactivity for the benzylic position was also affected for the diaryl-methanols and cyclic benzylic alcohol, which were effectively oxidized to the corresponding aryl ketones in high yields (Entries 4–8). By the present N_2O oxidation, the simple secondary alkanols, such as 4-phenyl-2-butanol, 2-undecanol and 4-decanol, could be converted to 4-phenyl-2-butanone, 2-undecanone and 4-decanone in 98%, 97%, and 89% yield, respectively (Entries 9–11). From cyclic alkanols, the corresponding products were obtained in high yields (Entries 12–14). When the reaction was applied to allylic alcohols, the corresponding epoxide was not obtained at all, and the corresponding α,β -

unsaturated ketone was selectively afforded in high yield (Entries 15 and 16). The primary benzylic alcohols were effectively converted into the corresponding arylaldehydes in high yields (Entries 17 and 18).¹² It should be pointed out here that any by-product such as carboxylic acid was not detected. Each reaction shown in Table 2 was monitored by TLC or GC analysis to confirm that the reaction proceeded with high selectivity.

Table 2. N₂O oxidation of various alcohols

Entry ^a	Substrates	Products	Yield /% ^c
1			92 ^d
2			94
3			quant
4			96
5 ^b			quant
6			99
7			99
8			95
9 ^b			98
10 ^b			97
11 ^b			89
12 ^b			97
13 ^b			86
14 ^b			97
15			89
16			quant
17			92
18			95 ^d

^aReaction conditions; 0.3 mmol of alcohols and 5.0 mol% of Ru(tmp)(O)₂ in 14 ml dichloroethane at 120 °C under 10 atm N₂O. ^bAt 150 °C. ^cIsolated yield. ^dGC yield.

It is noted that the selective oxidation of various alcohols to the corresponding ketones or aldehydes was effectively catalyzed by the dioxoruthenium porphyrin complex employing nitrous oxide (N₂O) as a terminal oxidant. The reaction proceeded smoothly with secondary and benzylic alcohols to give the corresponding ketones and aldehydes in high yields with high selectivity. It is expected that nitrous oxide could be a new terminal oxidant producing only N₂ gas as a by-product to provide a less wasteful process. A mechanistic study of the present reaction and further application of this oxidation system to other organic compounds are currently under investigation.

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- The optimum result using 1,2-dichloroethane was interesting for us because fluorobenzene was a suitable solvent for the N₂O epoxidation of olefins (fluorobenzene, 63% yield; dichloroethane, 40% yield of epoxide obtained, see Ref. 7). The reason for these observations is not quite obvious, though nitrous oxide is soluble in 1,2-dichloroethane the same as in other aromatic solvents.
- Typical procedure is as follows: To 1,2-dichloroethane solution of Ru(tmp)(O)₂ (13 mg, 0.015 mmol) in autoclave, a solution of 1-(2-naphthyl)ethanol (50 mg, 0.29 mmol) was added under a nitrous oxide atmosphere. After the solvent amount was controlled to be 14 ml, reaction mixture was heated to 120 °C under 10 atm of N₂O for 7.5 h. The produced ketone was obtained through silica-gel column with hexane/ether (10 : 1) mixture as the eluant (94% yield).
- When primary alcohols such as cinnamyl alcohol and 1-dodecanol were subjected to the oxidation, the corresponding aldehydes were obtained in 25–38% yields.