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Manganese-Catalyzed Selective Oxidation of Aliphatic C–H groups and Secondary Alcohols to Ketones with Hydrogen Peroxide

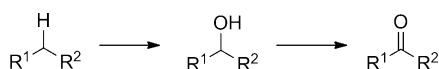
Jia Jia Dong,^[a] Duenpen Unjaroen,^[a] Francesco Mecozzi,^[a] Emma C. Harvey,^[a] Pattama Saisaha,^[a] Dirk Pijper,^[a] Johannes W. de Boer,^[b] Paul Alsters,^[c] Ben L. Feringa,^[a] and Wesley R. Browne*^[a]

An efficient and simple method for selective oxidation of secondary alcohols and oxidation of alkanes to ketones is reported. An in situ prepared catalyst is employed based on manganese(II) salts, pyridine-2-carboxylic acid, and butanedione, which provides good-to-excellent conversions and yields with

high turnover numbers (up to 10000) with H₂O₂ as oxidant at ambient temperatures. In substrates bearing multiple alcohol groups, secondary alcohols are converted to ketones selectively and, in general, benzyl C–H oxidation proceeds in preference to aliphatic C–H oxidation.

Introduction

Selective oxidation of alcohols to ketones together with direct conversion of C–H bonds to alcohols and ketones are crucial, yet also highly challenging, processes in synthetic organic chemistry, pharmaceuticals, and fine and bulk chemical synthesis (Scheme 1).^[1] Traditional methods for achieving such trans-



Scheme 1. Oxidation of alkanes and alcohols to ketones.

formations, although highly effective in general, are becoming increasingly undesirable because of rising demands to reduce environmental impact and increase the mass and energy efficiency of processes. Hence the drive to develop benign methods compels us to explore the use of methods using 1st row transition-metals and clean (mass-efficient) oxidants.^[2] Hydrogen peroxide is a highly favorable oxidant in this regard, second only to oxygen,^[3] with water as the sole by-product.^[4]

Several highly effective catalytic methods for the oxidation of alcohols with H₂O₂ have been reported, not least the system of Noyori and co-workers, based on tungsten oxide/PTC (where PTC is phase transfer catalyst),^[5] and the systems of Beller and co-workers, employing iron catalysts^[6] and catalysts based on rhenium, molybdenum, and tungsten oxides.^[7] However, the use of high temperatures and/or catalyst loadings and potentially toxic PTCs drives the search for alternative methods. Manganese-based catalysts are attractive in C–H and alcohol oxidations because of their generally low toxicity and the often high reaction rates and turnover numbers that can be achieved even at room temperature. Manganese catalysts, based on salen ligands^[8] have been employed in the oxidation of alcohols with iodosobenzene as oxidant^[8a] and catalyzed enantioselective kinetic resolution of secondary alcohols.^[8b]

Manganese catalysts based on polypyridyl and triazacyclononane-based ligands,^[9–11] as well as porphyrins,^[12] have also been applied.^[13]

Recently, our group reported an efficient method for the epoxidation and *cis*-dihydroxylation of alkenes catalyzed by an in situ prepared manganese(II) catalyst and which is near-stoichiometric in H₂O₂.^[14–16] This catalytic system consists of a Mn^{II} salt, pyridine-2-carboxylic acid, and sub-stoichiometric amounts of ketone, and showed good-to-excellent selectivity, high turnover numbers (up to 300 000) and high turnover frequencies (up to 30 s^{−1}) at room temperature, with a wide solvent scope.^[16]

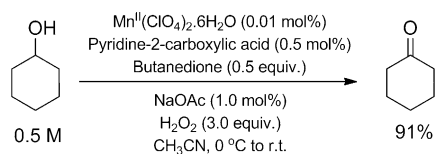
Here, we report the application of this catalytic system to the oxidation of alcohols and alkanes under ambient conditions and low catalyst loadings (Scheme 2). For substrates that do not bear alkene moieties, we show that high yields and selectivity can be achieved in the oxidation of secondary alcohols with good-to-excellent selectivity of secondary over primary alcohol oxidation. Furthermore, at higher catalyst loadings

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Scheme 2. Oxidation of cyclohexanol to cyclohexanone.

(0.1 mol%) selective C–H oxidation at benzylic positions can be achieved as well as C–H oxidation of alkanes.

Results and Discussion

In the present study, the oxidation of alcohols was initially investigated using conditions optimized earlier for alkene oxidation (Scheme 2),^[16] that is, using substrate (0.5 M), manganese perchlorate (0.01 mol%), sodium acetate (1.0 mol%), pyridine-2-carboxylic acid as catalyst (0.5 mol%), and butanedione (0.5 equiv. in acetonitrile) with H₂O₂ (1.5 equiv.). Under these conditions, cyclohexanol was oxidized to cyclohexanone in 73% yield, albeit with incomplete conversion (Table 1, entry 1). With 3.0 equiv of H₂O₂, full conversion and 91% yield of cyclo-

hexanone was obtained. Importantly, the reactions proceeded without formation of significant amounts of side products (e.g., Baeyer–Villiger oxidation products and double oxidation).

These conditions were applied to a series of secondary alcohols (Table 1). Cyclic and acyclic aliphatic alcohols were converted cleanly to their corresponding ketone products (Table 1, entries 2 and 3). For 5-nonanol, the conversion achieved was, however, lower, which was ascribed to its lower solubility in acetonitrile compared with the other alcohols examined. The relatively wide solvent scope of the present catalyst system, which was previously demonstrated,^[16] allows for the low solubility of 5-nonanol to be overcome by using acetone in place of acetonitrile and provided 5-nonanone in high yield (Table 1, entry 4).

The oxidation of sterically encumbered alcohols was also investigated. 2,4-dimethyl-pentan-3-ol was converted (71%) with 68% yield to 2,4-dimethyl-pentan-3-one (Table 1, entry 5). Similarly the natural product isborneol was converted to camphor in excellent yield (Table 1, entry 6). The reactions in general were found to be scalable, without significant difference in conversion or yield (see the Supporting Information for details). Notably, at larger scale, complete conversion was achieved by extraction of the product and unreacted starting material from the reaction mixture and subjecting the mixture to the same reaction conditions a second time. In the case of isborneol at a 4 g scale, full conversion and an isolated yield of 87% was achieved.

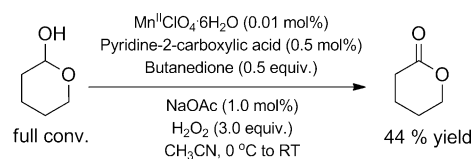
A series of secondary benzylic alcohols were oxidized to their corresponding ketones under these reaction conditions, in good yields (Table 1). Even bromo-phenyl or oxidatively sensitive methoxy-phenyl-bearing substrates proceeded in moderate-to-good conversion. In general, lower conversion can be overcome by decreasing the initial concentration of the substrate as with,^[16] for example, 1-(4'-methoxyphenyl)ethanol (Table 1, entry 11).

The oxidation of hemiacetals was explored through tetrahydro-2*H*-pyran-2-ol, which can be viewed as a cyclic alcohol with an ether functional group. Full conversion and moderate yield (44%) of valerolactone was achieved. The moderate yield of the desired product was primarily a result of the ring opening to generate the corresponding carboxylic acid in situ (Scheme 3).

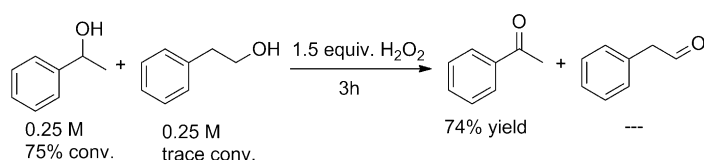
The selective oxidation of secondary aliphatic and aromatic alcohols in the presence of primary alcohols was explored through competition experiments (Schemes 4 and 5). Oxidation of an equimolar mixture of 1- and 2-phenyl-ethanol provided 75% conversion of 1-phenyl-ethanol to acetophenone with only trace conversion of 2-phenyl-ethanol. For substrates

Table 1. Oxidation of secondary alcohols. ^[a]				
Entry ^[a]	Substrate	Conv. ^[b] [%]	Product	Isolated Yield [%] ^[c]
1		full (73%)		91 ^[b] (73 ^[d])
2 ^[e]		full		78
3 ^[e]		97		88
4 ^[f]		80		72
5		71		68 ^[b]
6		full		95
7		97		90
8		92		77
9		90		80
10		88		75
11 ^[g]		70		64
12		78		76

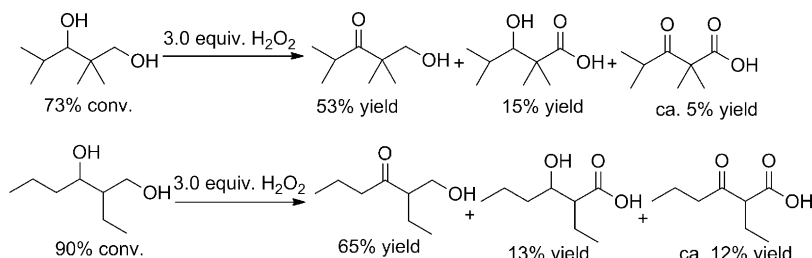
[a] Reaction conditions: 0.5 M substrate (1 mmol), 50 μM Mn(ClO₄)₂·6H₂O, 2.5 mM pyridine-2-carboxylic acid, 5.0 mM NaOAc, 0.25 M butanedione, and 1.5 M H₂O₂ in acetonitrile. [b] Conversion and yield, based on substrate, determined by ¹H NMR spectroscopy. [c] Isolated yield, unless stated otherwise. [d] 0.75 M H₂O₂ (1.5 equiv. with regard to substrate) was used. [e] 0.4 M substrate (0.8 mmol). [f] In acetone. [g] 0.25 M substrate (0.5 mmol).



Scheme 3. Oxidation of tetrahydro-2*H*-pyran-2-ol to valerolactone (yield determined by ¹H NMR spectroscopy).



Scheme 4. Competition experiment between 1-phenyl- and 2-phenyl-ethanol (for conditions, see Table 1).

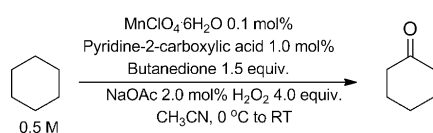


Scheme 5. Chemoselective oxidation of secondary over primary alcohol moieties (for conditions, see Table 1).

bearing both secondary and primary aliphatic alcohol moieties, oxidation of the secondary alcohol also proceeded preferentially (Scheme 5).

In addition to the oxidation of secondary alcohols to ketones, the direct oxidation of methylene units to ketones with the present catalytic system was explored.

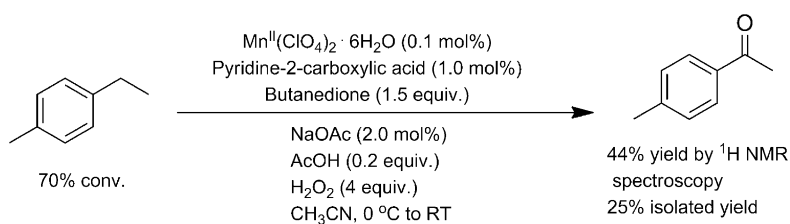
The direct oxidation of aliphatic compounds such as cyclohexane and cyclooctane proceeded with good conversion and selectivity to the corresponding mono-ketone product. (Table 2, entries 1 and 2). In contrast to alcohol oxidation, however, higher catalyst loadings (0.1 mol%) and up to 4.0 equiv. of H_2O_2 were required (Scheme 6). In addition to the ketone



Scheme 6. Oxidation of cyclohexane to cyclohexanone under optimized reaction conditions.

product, the corresponding alcohol, together with a mixture of diketones, was observed in amounts that were dependent on the exact reaction conditions.

At catalyst loadings of 0.1 mol%, the oxidation at the benzylic positions for a wide range of alkylated aromatics could be achieved at room temperature (Table 2, entries 3–12). For both ethylbenzene and propylbenzene, the corresponding aromatic ketone product was obtained with good selectivity (Table 2, entries 3 and 4). In con-



Scheme 7. Oxidation of 1-ethyl-4-methyl-benzene to 4-methyl-acetophenone under optimized reaction conditions.

trast, oxidation of toluene proceeded with lower conversion (35–40%) and low yield of a mixture of benzyl alcohol (8–10%), benzaldehyde (8–10%) and benzoic acid and with a low mass balance as a result of the formation of an insoluble polymeric material.

1-Ethyl-4-methyl-benzene was found to undergo good conversion (70%) with moderate yield of 4-methyl-acetophenone as the main product, albeit with significant amounts of a white polymeric by-product (Scheme 7). In general, for cyclic systems, full conversion was achieved with moderate-to-excellent isolated yields of the corresponding ketone (Table 2, entries 5–9). Surprisingly, in many cases, substantial amounts of the intermediate alcohol product were obtained, which would suggest that the rate of C–H oxidation, although slower, is nevertheless comparable with the rate of alcohol oxidation. The doubly oxidized product, anthracene-9,10-dione, was obtained from 9,10-dihydroanthracene in excellent yield, (Table 2, entry 7). In contrast, the mono-oxidized alcohol and ketone products were obtained as the primary product in the oxidation of 9,10-dihydrophenanthrene (Table 2, entry 9).

The selective oxidation of 1,2,3,4-tetrahydro-1-naphthol to the corresponding ketone, without further oxidation at the other benzylic position, confirms that benzylic positions are marginally less susceptible to oxidation than secondary aryl alcohols (Table 1, entry 10). Nevertheless, if there is sufficient oxidant available, further oxidation to the diketone products is observed.

p-Methoxy- and *o*-nitro-phenylethanes could be converted to the corresponding aryl-methyl-ketones as well (Table 2, entry 10 and 11). The lower yield of 1-(4-methoxy)phenyl-ethanone reflects the lower conversion also observed for the corresponding alcohol 1-(4-methoxyphenyl)ethanol (Table 1, entry 11). Similarly, lower conversion was observed for *o*-nitrophenylethane (Table 2, entry 11).

Surprisingly, oxidation of 2-benzyl-pyridine to phenyl(pyridin-2-yl)methanone proceeded with good conversion and selectivity without formation of the *N*-oxide product (Table 2, entry 12).

Table 2. Oxidation at alkyl and benzylic positions. ^[a]			
Entry	Substrate	Conv. [%]	Product/s (isolated yield [%]) ^[b]
1		63	(34 ^[c])
2		60	(41 ^[c])
3		80	(50 ^[c]) (13 ^[c])
4		50	(34) (3 ^[c])
5		full	(60) (12 ^[c]) (4 ^[c])
6		full	(66) (9 ^[c]) (25)
7		full	(99)
8 ^[d]		full	(76)
9		90	(37 ^[c]) (50 ^[c])
10		75	(28) (17 ^[c])
11		25	(17)
12		80	(73)
13		83	(34)

[a] Reaction conditions: 0.5 M substrate (1 mmol), 5 mM pyridine-2-carboxylic acid, 0.5 mM Mn(ClO₄)₂·6H₂O, 10 mM NaOAc, 0.75 M butanedione, and 2.0 M H₂O₂ in acetonitrile. [b] Isolated yield, based on substrate, unless stated otherwise. [c] ¹H NMR yield, based on substrate, see the Supporting Information for details. [d] 0.25 M substrate (0.5 mmol).

The selectivity towards methylene over methyl C–H groups was investigated using 1-methylpyrrolidin-2-one. Good conversion (83%) to and moderate isolated yield (34%) of 1-methylpyrrolidin-2,5-dione was achieved (Table 2, entry 13); however, the selectivity was poor with several side products also observed.

With regard to the mechanism for conversion of aliphatic C–H groups to alcohols and subsequently to ketones, it is likely that an active species similar to that previously reported in the oxidation of alkenes^[15,16] is responsible. The involvement of active oxygen species such as oxygen and hydroxyl radicals should also be considered, however. The direct involvement of atmospheric oxygen can be excluded based on mass balance; at the conversions observed, it would not be possible to obtain the oxygen required from the dissolved oxygen present. The disproportionation of the H₂O₂ present could provide con-

siderably more oxygen; however, this can also be discounted because of the relatively low level of catalase type activity observed. Hence, the presence of both alcohol and ketone products can be ascribed to sequential oxidation rather than, for example, a Russell's mechanism^[17] between alkyl radicals and oxygen.

Conclusions

Herein, we demonstrate that selective oxidation of secondary alcohols can be achieved at room temperature with an in situ prepared manganese catalyst with high turnover numbers (up to 10000) and with near stoichiometric amounts of H₂O₂. The reaction is scalable from 100 mg to 4 g and, in many examples, highly selective. Although we have demonstrated previously that this catalyst system is tolerant of several common protecting groups,^[16] the selectivity of the catalyst towards secondary alcohols over primary alcohols is also demonstrated, which reduces the need for the introduction prior to oxidation and subsequent removal of protecting groups and is complementary to catalytic methods for selective primary alcohol oxidation based on copper and TEMPO-based (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) catalysts.^[3c,6a] For benzylic alcohol oxidation and in particular for cyclic systems, selective oxidation to the monoketone product can be achieved under mild conditions and with good efficiency in terms of the oxidant H₂O₂.

Experimental Section

Caution: The drying or concentration of solutions that potentially contain H₂O₂ should be avoided. Prior to drying or concentrating, it is necessary to test for the presence of H₂O₂ by using peroxide test strips followed by neutralization on solid NaHSO₃ or another suitable reducing agent. When working with H₂O₂, suitable protective safeguards should be in place at all times.

Caution: Exposure to butanedione vapors has been linked with lung disease. It should be handled in a properly ventilated fumehood and exposure to vapors should be avoided.

General procedure for oxidation of secondary alcohols

The alcohol (1 mmol) was added to a stock solution containing Mn(ClO₄)₂·6H₂O (0.01 mol%, 0.0361 mg) and pyridine-2-carboxylic acid (0.5 mol%, 0.123 mg) in acetonitrile to generate a final substrate concentration of 0.5 M. NaOAc (aq. 0.6 M, 1 mol%, 16.7 μL) and butanedione (0.5 equiv., 43.5 μL) were added to generate a final volume of 2 mL. The solution was stirred with cooling in an ice/water bath before addition of H₂O₂ (50 wt%, 3.0 equiv., 170 μL). After 12–16 h stirring at room temperature, brine (10 mL) was added and the reaction was extracted with dichloromethane. The combined organic layers were reduced in vacuo. The products were isolated by flash column chromatography on silica gel of

230–400 mesh particle size. Products were characterized by NMR spectroscopy (see the Supporting Information).

General procedure for oxidation at alkyl and benzylic moieties C–H

The alkane (1 mmol) was added to a stock solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mol%, 0.361 mg) and pyridine-2-carboxylic acid (1.0 mol%, 0.246 mg) in acetonitrile to generate a final substrate concentration of 0.5 M. NaOAc (aq. 0.6 M, 2 mol%, 33.4 μL) and butanedione (1.5 equiv., 130.5 μL) were added to generate a final volume of 2 mL. The solution was stirred with cooling in an ice/water bath before addition of H_2O_2 (50 wt%, 4.0 equiv., 227 μL). After 12–16 h, brine (10 mL) was added and the reaction was extracted with dichloromethane (thrice 10 mL). The combined organic layers were reduced in vacuo. The products were isolated by flash column chromatography on silica gel of mesh particle size 230–400. Products were characterized by NMR spectroscopy (see the Supporting Information). In certain cases a solid material was also obtained, which, on the basis of FTIR, Raman, and NMR analysis, appeared to be a polymer.

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Keywords: alcohol oxidation · alkane oxidation · catalysis · manganese

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