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Bioorganic & Medicinal Chemistry Letters 17 (2007) 6364–6368
Bioorganic & Medicinal Chemistry Letters

Highly efficient selective oxidation of alcohols to carbonyl compounds catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride in the presence of molecular oxygen

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Received 6 July 2007; revised 19 August 2007; accepted 24 August 2007
Available online 28 August 2007

Abstract—Efficient selective oxidation of alcohols to carbonyl compounds by molecular oxygen with isobutyraldehyde as oxygen acceptor in the presence of metalloporphyrins has been reported. Ruthenium (III) *meso*-tetraphenylporphyrin chloride (Ru(TPP)Cl) showed excellent activity and selectivity for oxidation of various alcohols under mild conditions. Moreover, different factors influencing alcohols oxidation, for example, catalyst, solvent, temperature, and oxidant, have been investigated. In large-scale oxidation of benzyl alcohol, the isolated yield of benzaldehyde of 89% was observed.

Oxidation of alcohols to the corresponding carbonyl compounds is a very important step for organic synthesis.[1] From an environmental and cost-effective viewpoint, catalytic oxidation processes with molecular oxygen or air are extremely valuable and particularly attractive.[2] Accordingly, variety of transition metal based catalysts (mainly cobalt,[3] vanadium,[4] ruthenium,[5] palladium,[6] and copper[7]) have been intensively investigated for aerobic oxidation of alcohols so far.

As model catalysts of cytochrome P-450, metalloporphyrins could be used as the intermediate of oxygen carrier to biological systems, and have been widely used as catalysts for various oxidation reactions, for example, hydroxylation of hydrocarbon and epoxidation of olefins under mild conditions.[8] Although metalloporphyrins have been used to catalyze the oxidation of alcohols with PhIO,[9] Cl_2PyNO,[10] *t*-BuOOH,[11] $KHSO_5$,[12] Bu_4NHSO_5 (tetrabutylammonium peroxymonosulfate),[13] and *m*-CPBA (*m*-chloroperbenzoic acid)[14] as oxidants, few studies on metalloporphyrins-catalyzed oxidation of alcohols by molecular oxygen were reported.[15] For example, Woo and co-authors ever reported the aerobic homogeneous oxidation of benzyl alcohol with oxotitanium porphyrin (TTP)Ti=O, which gave benzaldehyde in modest yields (48%) after 94 h in refluxing chlorobenzene.[5a] Kato ever reported heterogeneous aerobic oxidation of benzyl alcohol by using microporous dinuclear ruthenium (II, III) carboxylate tetrafluoroborate containing porphyrin, $[Ru_2^{II,III}(H_2TCPP)]BF_4$($H_2TCPP$ = 4,4,4,4-(21H, 23H-porphine-5,10,15,20-tetrayl)tetrakis benzoic acid), as catalyst, in which high selectivity of benzaldehyde (95%) was obtained after 24 h and the TON (turnover number) of catalyst was 21.[15b]

In our previous studies, metalloporphyins exhibited high catalytic performance for oxidation of alkanes, olefins, and sulfides with molecular oxygen.[16] We also developed procedures for highly selective oxidation of alcohols to carbonyl compounds with β-cyclodextrin,[17] a ruthenium cation combined with microcrystals of cobalt hydroxide and cerium oxide[18] and nanoparticle spinel as catalysts.[19] As part of our ongoing interests in metalloporphyrins-catalyzed oxidations with dioxygen, the aerobic oxidation of alcohols to carbonyl compounds catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride (Ru(TPP)Cl) in the presence of isobutyraldehyde has been developed (Scheme 1).[20] The catalytic system has been proved to be efficient for oxidation of alcohols with high yields for carbonyl compounds under mild conditions.

The catalytic activity and selectivity of different metalloporphyrins for alcohol oxidation by molecular oxygen were investigated with benzyl alcohol as model com-

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Keywords: Ruthenium porphyrin; Alcohol; Carbonyl compound; Dioxygen.

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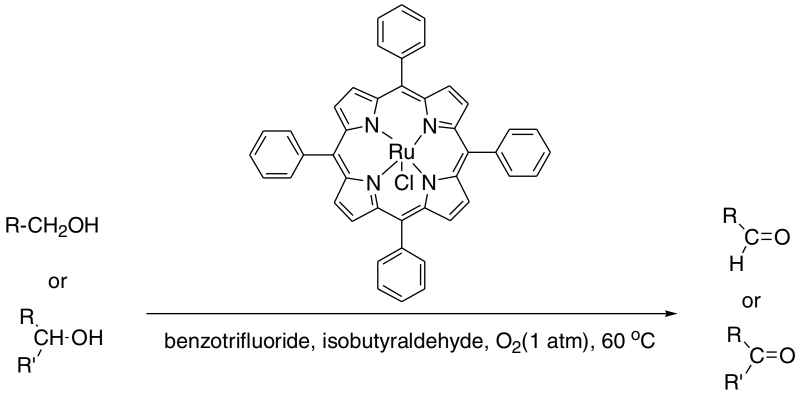
doi:10.1016/j.bmcl.2007.08.063



Scheme 1. Aerobic oxidation of alcohols catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride.

pound.[21] The engaged catalysts for the oxidation reactions were simple structural metalloporphyrins that have the same ligand, *meso*-tetraphenylporphyrin (TPP), but different metals including Ru(TPP)Cl, Co(TPP)Cl, Mn(TPP)Cl, and Fe(TPP)Cl. The results are summarized in Table 1.

From Table 1, the catalytic activity of metalloporphyrins appeared to be dependent on the nature of central ions for benzyl alcohol oxidation. Comparing with cobalt, manganese, and iron porphyrin, ruthenium porphyrin was the most effective catalyst for the alcohol oxidation system since benzyl alcohol could be completely converted to benzaldehyde. Cobalt porphyrin also presented similar high activity toward benzyl alcohol oxidation (entry 2), but poor selectivity for benzaldehyde was obtained after the reaction was carried out for 30 min. Similar results of alcohol oxidation were obtained with other cobalt catalysts, for example, Co(acac)$_3$[22] and cobalt Schiff base.[23] It seems that manganese and iron porphyrins were not effective catalysts for benzyl alcohol oxidation by molecular oxygen (entries 3 and 4). The catalytic activity and selectivity of different metalloporphyrins were probably influenced by stability of different valences of metal atoms and their electric potential.[24]

Aerobic oxidation of benzyl alcohol with Ru(TPP)Cl catalyst using various solvents and the effect of reaction temperature on its conversion were also investigated and the results are summarized in Table 2.

Table 1. Oxidation of benzyl alcohol by molecular oxygen in the presence of various metalloporphyrin catalysts[a]

Entry	Catalyst	Conv. (%)	Yield (%)[b]
1	Ru(TPP)Cl	>99	>99
2	Co(TPP)Cl	>99	42(58)[b]
3	Mn(TPP)Cl	45	33(12)[b]
4	Fe(TPP)Cl	32	32

[a] Benzyl alcohol (1 mmol), catalyst (1×10^{-3} mmol), isobutyraldehyde (3 mmol), benzotrifluoride (5 mL), O_2 bubbling (1 atm), 60 °C, 0.5 h.

[b] The numbers in parentheses indicate the yields of benzoic acid.

Table 2. The effect of solvent and temperature on the oxidation of benzyl alcohol by molecular oxygen in the presence of Ru(TPP)Cl[a]

Entry	Solvent	T (°C)	Conv. (%)	Yield (%)[b]
1	Benzotrifluoride	60	>99	>99
2	Benzotrifluoride	50	61	61
3	Benzotrifluoride	40	43	43
4	Toluene	60	73	61(12)
5	Benzene	60	74	60(14)
6	Acetonitrile	60	26	18(8)

[a] Benzyl alcohol (1 mmol), Ru(TPP)Cl (1×10^{-3} mmol), isobutyraldehyde (3 mmol), solvent (5 mL), O_2 bubbling (1 atm), 60 °C, 0.5 h.

[b] The numbers in parentheses indicate the yields of benzoic acid.

As shown in Table 2, it seemed that solvent played an important role in the oxidation system. The strong electrophilic effect of benzotrifluoride was favorable to the oxidation of benzyl alcohol, which gave 99% yield of benzaldehyde. When toluene and benzene were used instead, only about 60% benzaldehyde could be obtained, together with a little of benzoic acid. Very low yield of benzaldehyde (18%) could be obtained when acetonitrile was used as solvent in the oxidation system (entry 6). The distinct results should be attributed to the solvation effect of each solvent. The three fluorine atoms of the benzotrifluoride resulted in better solvation effect,[25] which could make the O–H bond cleavage much easier.

The effect of temperature on oxidation of benzyl alcohol was also investigated. It was shown that the conversion was increased with raising temperature from 40 to 60 °C. When the temperature was 60 °C, benzyl alcohol could be oxidized to benzaldehyde stoichiometrically by molecular oxygen with 1×10^{-3} mmol Ru(TPP)Cl catalyst. It is notable that the increasing temperature could hardly influence the selectivity of benzaldehyde, that is, no over-oxidation product, for example, benzoic acid could be detected as the temperature was raised.

The effects of oxidant on oxidation of benzyl alcohol were also investigated, and the results are summarized in Table 3. Table 3 shows that dioxygen was more effective than H_2O_2, *t*-BuOOH, and NaOCl for oxidation of benzyl alcohol catalyzed by Ru(TPP)Cl/isobutyraldehyde (entries 1, 4, 7, and 10), indicating that the metalloporphyrins have excellent performance for activating

Table 3. The effect of oxidant on the oxidation of benzyl alcohol catalyzed by molecular oxygen in the presence of Ru(TPP)Cl[a]

Entry	Oxidant	Conv. (%)	Yield (%)
1	O_2	>99	>99
2[b]	O_2	28	28
3[c]	O_2	<1	<1
4	H_2O_2	22	22
5[b]	H_2O_2	18	18
6[c]	H_2O_2	3	3
7	*t*-BuOOH	20	20
8[b]	*t*-BuOOH	26	26
9[c]	*t*-BuOOH	26	26
10	NaOCl	15	9
11[b]	NaOCl	13	6
12[c]	NaOCl	70	70

[a] Benzyl alcohol (1 mmol), Ru(TPP)Cl (1×10^{-3} mmol), isobutyraldehyde (3 mmol), benzotrifluoride (5 mL), 60 °C, 0.5 h, O_2 bubbling (1 atm), amount of H_2O_2, *t*-BuOOH, NaOCl was 2 mL, respectively.

[b] Without catalyst.

[c] Without isobutyraldehyde.

dioxygen due to their special structure. This could be further supported by the fact that the conversion was only 28% in the absence of catalyst (entry 2), while no obvious difference on catalytic activities could be observed with H_2O_2, *t*-BuOOH, and NaOCl as oxidants in the presence/absence of catalyst (entries 4/5, 7/8, and 10/11).

From Table 3, it could also be found that isobutyraldehyde played an important role in the benzyl alcohol oxidation system when dioxygen and hydrogen peroxide were employed as oxidants. The oxidation reaction with molecular oxygen stopped suddenly in the absence of isobutyraldehyde (entry 3). Similar phenomena could be observed for H_2O_2 oxidation system either, since the yield of benzaldehyde sharply decreased from 22% to 3% (entry 6). However, similar results could not be found for the oxidation system with *t*-BuOOH or NaOCl as oxidant in the absence of isobutyraldehyde. It should be attributed to the different formation mechanisms of high valent metal-oxo intermediates with different oxidants in the presence of isobutyraldehyde. In the case of dioxygen system, high valent metal-oxo intermediate was generated in the radical chain from isobutyraldehyde.[26] In addition, for the catalytic system with NaOCl as an oxidant, high yield of benzaldehyde could be obtained without isobutyraldehyde (entry 12). But only 15% of benzyl alcohol could be oxidized in the presence of isobutyraldehyde (entry 10). This is because that in the presence of isobutyraldehyde, isobutyraldehyde was preferentially oxidized to propanoic acid by the strong oxidant, which resulted in insufficient amount of oxidant for benzyl alcohol oxidation.

To evaluate the scope of the catalytic system, oxidation of various alcohols, including benzylic alcohols, secondary alcohols, and primary alcohols, by atmospheric dioxygen in the presence of Ru(TPP)Cl under mild conditions, has been investigated (Table 4).

As shown in Table 4, most alcohols could be smoothly converted to the corresponding aldehydes and ketones in high yields. It seems that the catalytic activity is dependent on the electronic property of substrates (entries 2–4). Secondary alcohols could be easily converted to the corresponding ketones in high yield (entries 5–8). In the case of 2-adamantanol, the catalytic system shows high activity, which gave ketone yield of 72% when the reaction continued for 30 min despite the hindrance. In the cases of saturated primary aliphatic alcohols, for example, 1-octanol and 1-hexanol, further oxidation of aldehydes to the corresponding carboxylic acids was observed under the same reaction conditions (entries 9 and 10). It is consistent with Han's result using *m*-CPBA (*m*-chloroperbenzoic acid) as oxidant and iron (III) porphyrin as catalyst.[14]

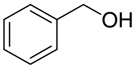
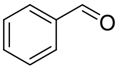
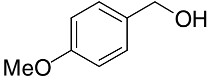
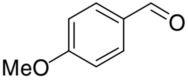
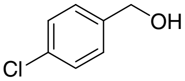
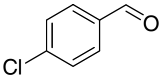
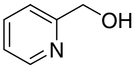
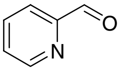
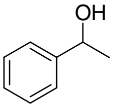
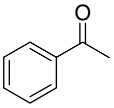
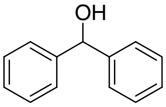
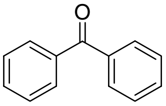
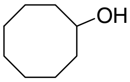
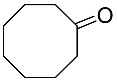
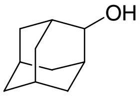
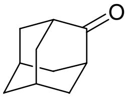
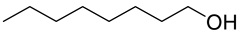
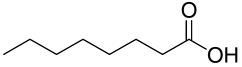
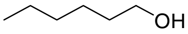
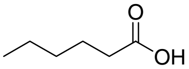
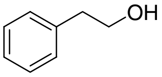
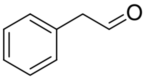
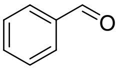
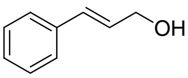
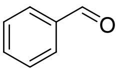
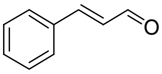
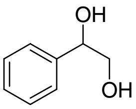
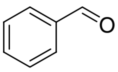
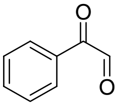
The alkyl length between benzene ring and –OH group could significantly influence the oxidation mode since only 27% of 2-phenylethanol was converted after running reaction for 30 min (entry 11). Furthermore, scission of C–C bond leading to loss of one methylene group was also observed in the oxidation of 2-phenylethanol, which gave a mean yield of phenylacetaldehyde and benzaldehyde. Similar C–C bond cleavage could also be found when cinnamyl alcohol was subjected to the reaction system (entry 12), in which, cinnamyl alcohol could be converted completely and benzaldehyde was the main product owing to the existence of C=C bond. The catalytic system also exhibited high activity for the oxidation of diol, for example, 1-phenyl-1,2-ethanediol (entry 13). The main product benzaldehyde resulted from the oxidative cleavage of C–C bonds. Diols that could be cleaved by molecular oxygen to the corresponding aldehydes were also reported with $Ru(PPh_3)_3Cl_2$ as catalyst.[27] Okamoto reported that an alkoxide was the intermediate in 1,2-diol oxidation in the presence of molecular oxygen.[28] So, in the present study of C–C bond cleavage, alkoxide complex was formed by the reaction of alcohol with high valent Ru(V) porphyrin. Then the carbonyl product could be formed by the thermal decomposition of alkoxide.

A large-scale oxidation of benzyl alcohol was carried out in the presence of molecular oxygen as shown in Scheme 2.[29]

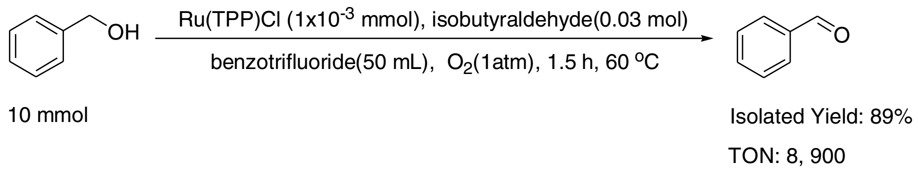
When the amount of Ru(TPP)Cl catalyst was 1×10^{-3} mmol, benzaldehyde could be obtained with the isolated yield of 89% by conducting the reaction for 1.5 h. It should be mentioned that the turnover number of the present catalyst could reach up nearly nine thousand.

Conclusions. In conclusion, ruthenium (III) *meso*-tetraphenylporphyrin chloride has been proven to be an excellent catalyst for oxidation of alcohols in the presence of molecular oxygen and isobutyraldehyde. All the factors that effected benzyl alcohol oxidation were well investigated. Various alcohols including benzylic alcohols, primary alcohols, and secondary alcohols could be successfully oxidized.

Table 4. Oxidation of various alcohols by molecular oxygen in the presence of Ru(TPP)Cl[a]

Entry	Alcohol	Product	Time (h)	Conv. (%)	Yield (%)
1			0.5	>99	>99
2			1.0	35	35
3			0.5	91	91
4			1.0	17	17
5			0.5	94	94
6			1.5	93	93
7			1.0	94	94
8			0.5	91	72
9			1.0	93	71
10			1.0	90	70
11			0.5	27	14
					13
12[b]			1.0	100	74
					17
13			0.5	>99	88
					8

[a] Substrate (1 mmol), Ru(TPP)Cl (1×10^{-3} mmol), isobutyraldehyde (3 mmol), benzotrifluoride (5 mL), O_2 bubbling (1 atm), 60 °C, 0.5 h.
[b] Toluene (5 mL) as solvent.



Scheme 2. Large-scale aerobic oxidation of benzyl alcohol by molecular oxygen in the presence of Ru(TPP)Cl.

Acknowledgments

The authors thank the National Natural Science Foundation of China (20576045) and the Program for New Century Excellent Talents in University (NCET-06-740) for providing financial support for this project.

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