Heteroatom Chemistry
Volume 23, Number 3, 2012

Rapid Aerobic Oxidation of Alcohols to Carbonyl Compounds with Dioxygen Using Metallodeuteroporphyrin Dimethyl Esters as Catalysts in the Presence of Isobutylaldehyde

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Received 23 October 2011; revised 9 January 2012, 13 February 2012

ABSTRACT: *A facile biomimetic method for rapid oxidation of alcohols to carbonyl compounds using dioxygen as the primary oxidant catalyzed by metallodeuteroporphyrin dimethyl ester [M(DPDME)] in acetonitrile as the reaction solvent and isobutylaldehyde as cocatalyst has been investigated. Among the M(DPDME) catalysts, where M = Fe(III), Co(II), Mn(III), Ni(II), Cu(II), and Zn(II), cobalt porphyrin was found to be the most active and effective catalyst. The catalytic system was widely used in the oxidation of various alcohols and especially exhibited excellent activity for oxidation of aromatic alcohols under mild conditions. Moreover, M(DPDME) was prepared from an improved facile method by chemical modification of natural hemin and an alternative mechanism for the aerobic oxidation of alcohols has been proposed and discussed.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 23:295–303, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21017

INTRODUCTION

Aerobic oxidation of alcohols into the corresponding aldehydes and ketones is one of the fundamental and important reactions in organic synthesis as well as in the chemical industry for the synthesis of drugs, insecticides, and fragrances [1,2]. In the past decades, many efficient catalytic oxidation systems have been developed, including various oxygen transfer reagents in the presence of noble metal catalysts, such as gold [3], vanadium [4], palladium [5], ruthenium [6], Cu/Nb_2O_5 and Ag/Ni fiber [7], and hazardous or toxic oxidizing agents [8,9]. In the wake of increasing concern about the environment and economy, catalytic oxidation processes are thus extremely valuable; in particular, employing dioxygen (air) and nonnoble metal catalysts is particularly attractive. However, a few efficient, aerobic oxidations are known that proceed under mild conditions and are amenable to the preparation of fine chemicals [10].

P450 enzymes have been found to efficiently catalyze the oxidation of organic substrates by binding or activating dioxygen under very mild conditions with the help of the heme [iron(III) protoporphyrin-IX] prosthetic group [11]. Depending on the function performed, metalloporphyrins have been synthesized and used as models of cytochrome P450 enzymes for various oxo transfer reactions, such as hydroxylation of alkanes, epoxidation of alkenes, oxidation of heteroatoms, dealkylation reactions, and oxidation of aromatics. In particular, selective oxidation of alcohols catalyzed by metalloporphyrins has been widely studied in the presence of various oxygen atom donors, such as *m*-CPBA [12], $NaIO_4$ [13], Bu_4NHSO_5 [14], *t*-BuOOH [15],

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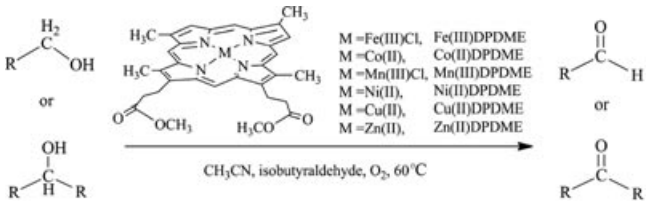
Contract grant sponsor: Jiangsu Natural Science Foundation.
Contract grant number: BK2009386.
Contract grant sponsor: Jiangsu Graduate Innovation Project.
Contract grant number: CXZZ11_0263.

H_2O_2, and PhIO [16]. However, there have been few reports on the selective aerobic oxidation of alcohols using dioxygen. In 2000, Du and Woo reported that oxotitanium porphyrin (TTP)Ti=O catalyzed the aerobic oxidation of diols to ketones or aldehydes in modest yields [17]. Subsequently, Ji and coworkers revealed that Ru(III)TPP could effectively catalyze selective oxidation of benzyle alcohols to carbonyl compounds in the presence of isobutylaldehyde as cocatalyst under mild conditions [18]. Recently, Rahimi et al. have found that Cu(II)TPP is an effective catalyst for the transformation of benzyl alcohols to benzaldehydes using the above systems [19].

However, all of these above-mentioned metalloporphyrins are usually related to the synthetic porphyrins (tetraarylporphyrin). Metallodeuteroporphyrin dimethyl esters [M(DPDME)s], derived from the natural hemin, have never been reported for the selective aerobic oxidation of alcohols. Our previous study has demonstrated that M(DPDME)s are very effective catalysts for the oxidation of cyclohexane with air in the absence of additives and solvents [20]. On the basis of these facts and considerations, the natural hemin derivatives M(DPDME)s, where M = Fe(III), Co(II), Mn(III), Ni(II), Cu(II), and Zn(II), have attracted our attention to investigate their activities in the oxidation of alcohols using dioxygen under mild conditions (Scheme 1).



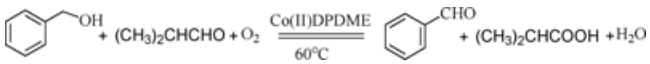
SCHEME 1 M(DPDME)-Catalyzed oxidation of alcohols by dioxygen in the presence of isobutylaldehyde.

RESULTS AND DISCUSSION

Optimization of Reaction Conditions

For the initial experiments, benzyl alcohol was selected as the substrate and reacted in acetonitrile under a stream of oxygen, with small quantities of Co(II)DPDME, in the presence of isobutylaldehyde. The results of these studies are collected in Table 1, which shows that the reaction temperature has a significant effect on the yields and reaction rates in this system (Table 1, entries 1–3). At nearly room temperature, the conversion of benzyl alcohol to the corresponding aldehyde was very low, and for a moderate oxidation activity, the reaction temperature needed to be around 60°C. It is worthwhile to note that increasing temperature would not result in the transformation of benzaldehyde into benzoic acid in the range of 30–60°C.

TABLE 1 Co(II)DPDME-Catalyzed Oxidation of Benzyl Alcohol[a]



Entry	*Solvent*	*Temperature (°C)*	*Time (min)*	*Conversion (%)*	*Yield[b] (%)*
1	Acetonitrile	30	60	5	5
2	Acetonitrile	40	40	61	61
3	Acetonitrile	60	40	>99	>99
4	Acetone	60	60	>99	46(54)[c]
5	Pyridine	60	90	<1	<1
6	Chloroform	60	70	75	70(5)[c]
7	Benzene	60	50	95	65(30)[c]
8	*n*-hexane	60	80	70	58(12)[c]
9[d]	Acetonitrile	60	40	<10	<10
10[e]	Acetonitrile	60	40	3	3
11[f]	Acetonitrile	60	40	1	1
12[g]	Acetonitrile	60	40	30	30

[a]Benzyl alcohol (1 mmol), Co(II)DPDME (0.01 mmol), isobutylaldehyde (3 mmol), solvent (6 mL), O_2 bubbling (1 atm).
[b]GC/MS yield based on the starting alcohol.
[c]The yield of benzoic acid.
[d]One mmol of imidazole was added.
[e]One mmol of *N*-phenyl-1-naphthylamine was added.
[f] In the absence of isobutylaldehyde.
[g]In the absence of Co(II)DPDME.

TABLE 2 Oxidation of Benzyl Alcohol Catalyzed by M(DPDME) in the Presence of Dioxygen[a]

Entry	Catalyst	Time (min)	Conversion (%)	Yield[b] (%)
1	Co(II)DPDME	40	>99	>99
2	Mn(III)DPDME	40	86	84
3	Cu(II)DPDME	60	80	80
4	Fe(III)DPDME	60	58	56
5	Ni(II)DPDME	60	34	33
6	Zn(II)DPDME	60	14	14

[a]Benzyl alcohol (1 mmol), catalyst (0.01 mmol), isobutylaldehyde (3 mmol), CH_3CN (6 mL), 60°C, O_2 bubbling (1 atm).
[b]GC/MS yield based on the starting alcohol.

To further optimize the aerobic oxidation in organic solvent, different properties of solvents were used in the oxidation of benzyl alcohol, resulting in an unexpected conversion and selectivity. Among all the solvents studied, acetonitrile was the most suitable for the reaction, giving an overall yield of more than 99% for benzaldehyde. Although the excellent conversion was obtained in acetone or benzene with a prolonged time, the corresponding benzoic acid was produced in the oxidation process, leading to lower selectivity and therefore lower yield of benzaldehyde (Table 1, entries 4, 7). When chloroform and *n*-hexane were used instead, about 70% conversion could be obtained, together with a small amount of benzoic acid (Table 1, entries 6, 8). Unfortunately, when pyridine was employed as solvent, the reaction did not proceed catalytically (Table 1, entry 5). Next, a control experiment of the oxidation of benzyl alcohol with Co(II)DPDME was conducted at 60°C in acetonitrile for 40 min in the presence of imidazole that resulted in less than 10% yield of benzaldehyde (Table 1, entry 9). This result suggested that the aerobic oxidation proceeds were affected by the solvent effect, pyridine disfavored formation of the oxygenated metalloporphyrins species. From another point of view, imidazole was similar to the radical inhibitor and the reaction was indeed inhibited. We also studied the effect of addition of the free radical inhibitor *N*-phenyl-1-naphthylamine [21] and found that the oxidizing reaction was indeed inhibited by its presence (Table 1, entry 10). The results suggested that the catalytic process occurred by the free radical chain mechanism in the case of dioxygen and isobutylaldehyde [21]. In addition, the oxidation of benzyl alcohol in the absence of isobutylaldehydeor or Co(II)DPDME catalyst proceeded slowly and led to the low yield of benzaldehyde after 60 min in acetonitrile (Table 1, entries 11, 12).

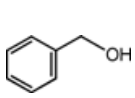
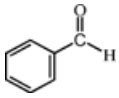
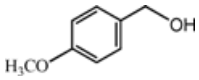
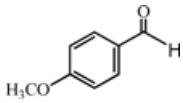
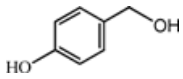
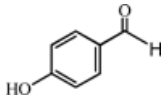
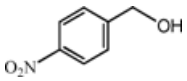
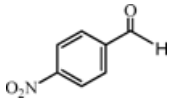
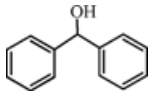
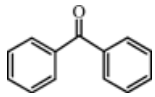
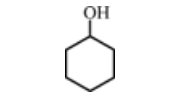
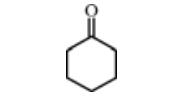
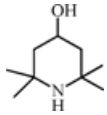
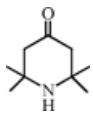
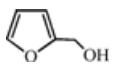
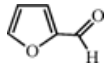
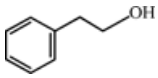
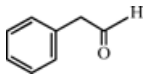
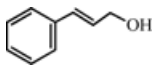
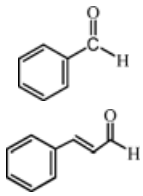
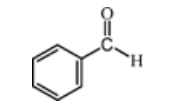
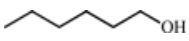
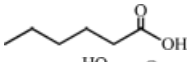
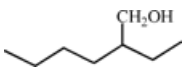
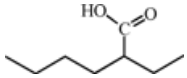
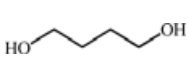
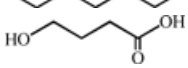
Investigation of the Activity of M(DPDME)

Under the above-optimized reaction conditions, the catalytic activity of various M(DPDME), where M = Fe(III), Co(II), Mn(III), Ni(II), Cu(II), and Zn(II), was investigated for the oxidation of benzyl alcohol to carbonyl compounds by dioxygen. As shown in Table 2, the oxidation of benzyl alcohol catalyzed by these catalysts produced benzaldehyde as the main product and the catalytic activity of metalloporphyrins seemed to be dependent on the nature of central metal ions incorporated into the porphyrin center for benzyl alcohol oxidation. Among the six simple structure metalloporphyrin catalysts, Co(II)DPDME was found to be the best efficient catalyst. Mn(III)DPDME and Cu(II)DPDME also exhibited high activity toward benzyl alcohol oxidation. To our surprise, Zn(II)DPDME presented poor catalytic performance, which was much weaker than that observed for the oxidation of benzyl alcohol without metalloporphyrin catalyst (Table 1, entry 12). The poor catalytic activity of Zn(II)DPDME more likely may be due to its lack of accessibility to higher oxidation states. Therefore, the metal property was responsible for the lower level of benzaldehyde formation. More specifically, the different activities of metalloporphyrins were observed with the following reactivity order: Co(II)DPDME > Mn(III)DPDME > Cu(II)DPDME > Fe(III)DPDME > Ni(II)DPDME > Zn(II)DPDME. A reason can explain the trend, possibly due to the fact that the stability of different valences of metal atoms and their electric potential played a crucial role in the catalytic activity of different metalloporphyrins [22].

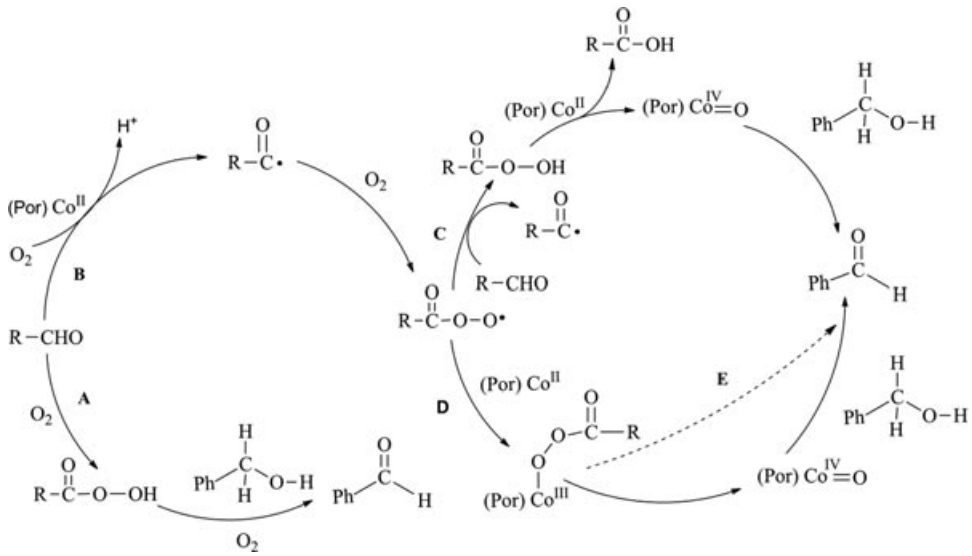
Oxidation of Various Alcohols

To check the generality of this method, the scope of this optimized procedure for the oxidation of various alcohols is indicated by the results listed in Table 3. It is noteworthy that aromatic alcohols were smoothly converted to the corresponding aldehydes in excellent conversion, and the yield was more than 92% in all cases (Table 3, entries 1–4). It is concluded that this catalytic system shows the tolerance of a variety of substituents on aromatic nuclei. Secondary alcohols were also easily oxidized to the corresponding ketones in good yields with any overoxidation by-products (Table 3, entries 5–7). For example, benzhydrol gave benzophenone with 100% yield for 30 min, irrespective of steric factors in the alcohols. However, the reaction for oxidation of 2,2,6,6-tetramethyl-4-piperidinol was relatively slow and the corresponding ketone was obtained in only 8% yield even after 60 min (Table 3, entry 8). A

TABLE 3 Co(II)DPDME-Catalyzed Oxidation of Various Alcohols[a]

Entry	*Substrate*	*Product*	*Time (min)*	*Conversion (%)*	*Yield[b] (%)*
1			40	>99	>99
2			30	>99	92
3			30	>99	95
4			60	95	95
5			30	100	100
6			30	70	70
7			90	85	85
8			60	8	8
9			30	11	11
10			60	47	25
11			60	100	22 35
					8 57
12			30	52	41
13			30	45	34
14			30	30	30

[a]Substrate (1 mmol), CoDPDME (0.01 mmol), isobutylaldehyde (3 mmol), CH_3CN (6 mL), 60°C, O_2 bubbling (1 atm).
[b]GC/MS yield based on the starting alcohol.



SCHEME 2 Plausible mechanism for the oxidation of benzyl alcohol catalyzed by Co(II)DPDME in the presence of isobutylaldehyde and dioxygen.

surprised result was obtained in the oxidation of furfuryl alcohol under the same conditions (Table 3, entry 9). This phenomenon was consistent with the above study of using pyridine as a solvent. Unfortunately, this catalytic system is incompatible with a range of heteroatoms, including nitrogen and oxygen heterocycles.

It is interesting to note that the oxidation of 2-phenylethanol produced two products (Table 3, entry 10) due to the scission of a C—C bond leading to loss of one carbon atom, which were confirmed by GC/MS analysis. Similar C—C bond cleavage could be found in the oxidation of cinnamyl alcohol; in addition, the end product was still an aldehyde without any further oxidation to the corresponding acid. However, an expected result occurred in the epoxidation of C=C bond when the cinnamyl alcohol was converted completely into aldehyde (Table 3, entry 11). Furthermore, the catalytic system also exhibited high selectivity for the oxidation of aliphatic to carboxylic acid (Table 3, entries 12, 13), although the conversion was relatively low by comparison with the oxidation of aromatic alcohol, for instance, 1,4-butanediol (Table 3, entry 14).

Plausible Mechanism for the Oxidation of Benzyl Alcohol Catalyzed by Co(II)DPDME

For metalloporphyrin-catalyzed oxidation reactions of various organic compounds, the application of metalloporphyrins in combination of peroxides (such as *t*-BuOOH and *m*-CPBA) was intensively studied. It is suggested that a reaction of peroxide with metalloporphyrins resulted in the formation of high-valent metal oxoporphyrin species or metalloporphyrin π-radical cations. In the present oxidation of benzyl alcohol catalyzed by Co(II)DPDME, [M(DPDME)s] were essential for the reaction in the presence of isobutylaldehyde plus dioxygen.

Based on all the above-mentioned results, a plausible reaction pathway for the conversion of benzyl alcohol to the corresponding benzaldehyde catalyzed by Co(II)DPDME with dioxygen in the presence of isobutyraldehyde is depicted in Scheme 2. Consistent with this picture, in the absence of Co(II)DPDME, the oxidation of benzyl alcohol can occur in a noncatalytic radical pathway (Scheme 2, pathway A), giving a small amount of benzaldehyde under our experimental conditions (Table 1, entry 12). However, an apparent exception to this route occurred when the metalloporphyrins were added to the reaction mixture. According to the literature [21,23], the mechanism that has been proposed for the metal complex–catalyzed oxygenation of substrates by O_2 and aldehyde is a free radical chain mechanism, in which the metal complex reacts with aldehyde to generate an acyl radical (RC(O)) (Scheme 2, pathway B). The acyl radical then reacts with O_2 to give an acylperoxy radical (RC(O)OO) that is an important intermediate. Subsequently, two different suggestions for the formation of a high-valent cobalt-oxo species $[(Por)Co^{IV}=O]^{\bullet+}$ have been made in this study. On the one hand, the acylperoxy radical acts as a carrier in a chain mechanism by reacting with another aldehyde molecule to give the peroxyacid, thereby generating another acylradical. The high-valent cobalt-oxo species are produced by the reaction of the peroxyacid with Co(II)DPDME

catalyst, which have been evoked as active key intermediates and are responsible for oxygen atom transfer in the alcohol oxidation reactions (Scheme 2, pathway C). For this reason, in a control reaction, tert-butyl hydroperoxide (5 mmol) was slowly added to a solution containing benzyl alcohol (1 mmol) and Co(II)DPDME (0.01 mmol) in CH_3CN (6 mL). The reaction was stirred at 60°C for 30 min under O_2; only 28% yield of the benzaldehyde was detected based on GC/MS analysis. The results are in accordance with that generally shown in the existing literature [18]. But the investigation produced results that suggested that the oxidation reaction did not fully proceed by the route described in pathway C. On the other hand, the second suggestion is that $RC(O)OO^{\bullet}$ binds Co(II)DPDME to form a cobalt porphyrin–peroxy complex [$(Por)Co^{III}$—$OOC(O)R$]. In pathway D, the cobalt porphyrin–peroxy complex can form the $[(Por)Co^{IV}{=}O]^{\bullet+}$ by the oxygen–oxygen bond cleavage of the peroxy group, resulting in a high conversion of benzyl alcohol. Therefore, the presence of cobalt-oxo porphyrin was confirmed by in situ UV–vis spectra for the oxidation of benzyl alcohol. As shown in Fig. 1, the initial Soret absorption peak of Co(II)DPDME was at 414 nm. After adding aldehyde, benzyl alcohol, and feeding dioxygen into the reaction system, in situ determination revealed that the characteristic absorption peak of Co(II)DPDME weakened gradually. The results suggested the conversion of Co(II)DPDME to other active species [24]. In addition, the Soret absorption peak at 414 nm is quite decreased, which may be affected by the active species. As discussed above, we suggested that the pathway from B to D for the oxidation of alcohol appeared to be the best catalytic process in light of the experimental results. Such a mechanism proposed in this study is reminiscent of the mechanism proposed by Nam et al. in the metal-complex-catalyzed epoxidation of olefins with dioxygen plus aldehydes [21].

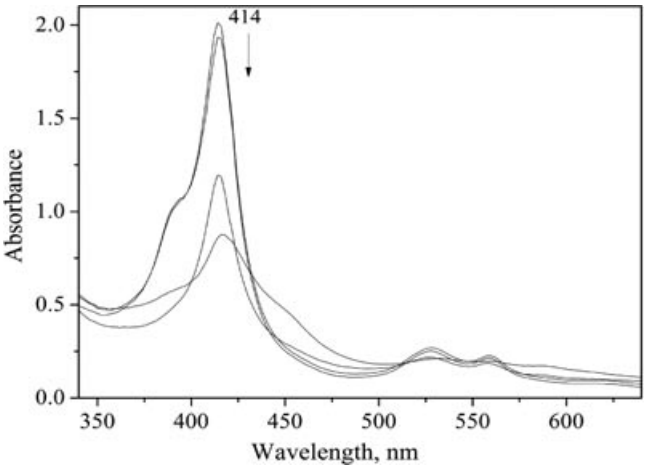


FIGURE 1 UV–vis spectra of Co(II)DPDME in the solution of benzyl alcohol oxidation in the presence of isobutyraldehyde and dioxygen (time scan: 0, 5, 15, 25 min).

EXPERIMENTAL

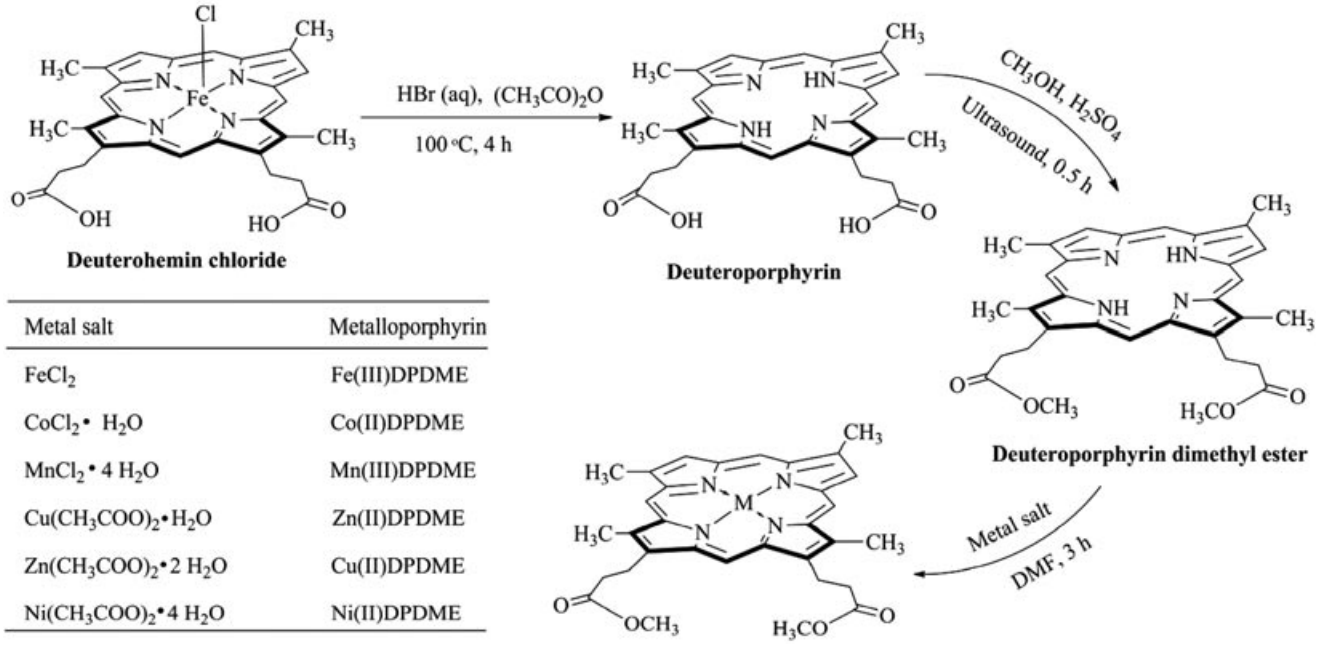
Apparatus and Materials

^1H NMR was recorded on a Bruker 500 MHz spectrometer (Bruker Biospin, Rheinstetten, Germany) with tetramethylsilane as an internal standard. MS/MS (ESI) mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer (Thermo Finnigan, San Jose, CA). The UV–vis spectra were measured on a Shimadzu UV-240 spectrophotometer (Shimadzu , Kyoto, Japan). IR spectra were obtained by a Perkin–Elmer 681 instrument with KBr optics (Perkin-Elmer, Boston, MA). GC/MS analyses were performed on a Thermo Trace DSQ mass spectrometer (Thermo Finnigan) under the following conditions. Helium was used as carrier gas at a flow rate of 1.2 mL min^{-1}. GC was conducted using an RTX-5MS column (15 m × 0.25 mm × 0.25 mm, Restek Corporation, Bellefonte, PA). The column temperature was programmed from 40°C (1.5 min hold) to 260°C at 15°C min^{-1}. The injector temperature was set at 220°C with a split ratio of 15:1. Both interface temperature and ion source temperature were set at 250°C. The column outlet was inserted directly into the electron ionization source block, operating at 70 eV.

Deuteroporphyrin dimethyl ester was prepared from the improved methods, as described in Scheme 3, and its metal complexes were synthesized by the reaction of DPDME with metal salts according to the procedure of Adler et al. [25]. Products were characterized by MS/MS and UV–vis, as shown in Table 4. The synthesis of DPDME involved two steps: demetalation of deuterohemin by the mixture of glacial acetic anhydride and concentrated hydrobromic acid and esterification of deuteroporphyrin with CH_3OH/H_2SO_4 (trace) with ultrasonic acceleration of the reaction instead of using the complicated, time-consuming, low-yield producing methods, such as Fe/HCOOH, H_2SO_4/CF_3COOH, $HCl_{(gas)}/FeSO_4/AcOH/CH_3OH$, and $HBr_{(gas)}$/AcOH [26–30]. Deuterohemin chloride was synthesized as previously described from hemin [28]. Other chemicals were commercially available and used as received without further purification.

Preparation of Deuteroporphyrin

A solution of 26 mL of acetic anhydride in a 150-mL of three-neck flask was cooled to 5°C and



Metal salt	Metalloporphyrin
$FeCl_2$	Fe(III)DPDME
$CoCl_2 \cdot H_2O$	Co(II)DPDME
$MnCl_2 \cdot 4\,H_2O$	Mn(III)DPDME
$Cu(CH_3COO)_2 \cdot H_2O$	Zn(II)DPDME
$Zn(CH_3COO)_2 \cdot 2\,H_2O$	Cu(II)DPDME
$Ni(CH_3COO)_2 \cdot 4\,H_2O$	Ni(II)DPDME

SCHEME 3 Preparation of metallodeuteroporphyrin dimethyl ester.

TABLE 4 MS/MS Analysis and UV–Vis Spectra of DPDME and Its Metal Complexes in CH_3CN

		UV–Vis	
Metalloporphyrin	*MS/MS (m/z) (Fragment)*	*Soret/λ, nm (log ε)*	*Q/λ, nm (log ε)*
DPDME	ESI$^+$–MS (40 ev): $m/z = 539.11$ $[M + H]^+$, 524.10, 465.06, 451.05, 407.06, 393.03, 379.01	396 (3.61)	496 (2.92), 528 (2.88), 564 (2.80), 6 18 (2.72)
Co(II)DPDME	ESI$^+$–MS (30 ev): $m/z = 594.95$ $[M]^+$, 521.95, 507.95, 448.91	414 (3.49)	527 (2.66), 559 (2.58)
Mn(III)DPDME	ESI$^+$–MS (45 ev): $m/z = 590.96$ $[M]^+$, 517.94, 502.95, 458.96, 444.93	365 (3.41)	456 (3.36), 543 (2.66)
Cu(II)DPDME	ESI$^+$–MS (35 ev): $m/z = 598.95$ $[M]^+$, 525.97, 511.91, 452.89	396 (3.74)	522 (2.55), 558 (2.71)
Fe(III)DPDME	ESI$^+$–MS (40 ev): $m/z = 591.98$ $[M]^+$, 518.98, 504.97, 445.98	388 (3.64)	533 (2.60)
Ni(II)DPDME	ESI$^+$–MS (40 ev): $m/z = 594.96$ $[M]^+$, 521.94, 488.94, 448.87, 434.91	389 (3.73)	512 (2.66), 547 (2.99)
Zn(II)DPDME	ESI$^+$-MS (35 ev): $m/z = 600.08$ [M]+, 526.89, 511.84, 454.05	406 (3.78)	536 (2.85), 573 (2.75)

then 5 mL of concentrated hydrobromic acid was added in dropwise fashion under the condition of mechanical stirring. After addition was complete, deuterohemin chloride (2.0 g, 3.34 mmol) was added to the flask and the reaction was warmed to 100°C for 4 h. At the end of this period, the reaction was quenched with NaOH (2.0 mol L^{-1}) until the pH was 5.0–6.0. The as-obtained brown precipitate was filtrated and washed with distilled water. The residue was recrystallized from hot acetone and dried in vacuum at 100°C for 3 h to give 1.6 g (3.13 mmol, 93.95%) of deuteroporphyrin as brown solid: mp >300°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = −4.03 (s, 2H), 3.27–3.30 (t, J = 11.50 Hz, 4H, $2CH_2$), 3.63–3.77 (4s, 12H), 4.40–4.43 (t, J = 11.50 Hz, 4H, $2CH_2$), 9.33, 9.35 (2s, 2H), 10.30, 10.33, 10.35, 10.36 (4s, 4H), 12.1 (s, 2H). IR (KBr, cm^{-1}): 3460 (m, N–H), 2916 (m, OH), 1725 (s, C=O), 1435 (m), 1361 (m), 1300 (w), 1235 (w), 1196 (m), 1165 (s, C–O), 1125 (m), 894 (w). UV–vis (DMF): λ_{max}(log

ε), 398 (3.61), 496 (2.59), 528 (2.47), 565 (2.28), 619 (2.20). ESI^+–MS (45 ev), m/z = 509.16 $[M - H]^-$, 447.09 $[M{-}H{-}2CH_3{-}2OH]^-$, 432.06 $[M{-}H{-}CH_2{-}CH_2COOH]^-$, 421.12 $[M{-}H{-}CH_3{-}CH_2\ CH_2\ COOH]^-$, 406.90 $[M{-}H{-}2CH_3{-}CH_2CH_2COOH]^-$, 378.07$[M{-}\ H{-}4CH_3{-}CH_2CH_2COOH]^-$.

Preparation of Deuteroporphyrin Dimethyl Ester

To the mixture of deuteroporphyrin (1.0 g, 1.96 mmol) and excess alcohol (0.30 mol) in a boiling flask of 150 mL, concentrated H_2SO_4 (0.1 mL) was added as catalyst at room temperature in an ultrasound bath having a frequency of 40 kHz. After the addition, the mixture was irradiated by ultrasound for 0.5 h, and then extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4. After solvent removal, the residue was further purified by column chromatography on silica gel (dichloromethane:ethyl acetate = 10:1) to afford 0.9 g (1.67 mmol, 85.38%) of deuteroporphyrins dimethyl ester as brick-red solid: mp 224–225°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = −3.87 (s, 2H), 3.30, 3.29, 3.27 (t, J = 7.25, 4H), 3.73, 3.75 (2s, 6H), 3.63–3.66 (4s, 12H), 4.41, 4.42, 4.44 (t, J = 7.25, 4H), 9.08, 9.09 (2s, 2H), 10.03, 10.07, 10.10, 10.13 (4s, 4H). IR (KBr, cm^{-1}): 3400 (m, N—H), 2900 (w), 1733 (s, C=O), 1435 (m), 1361 (m), 1300 (w), 1235 (w), 1196 (m), 1165 (s, C—O), 1125 (m), 1055 (w), 1016 (m), 970 (m), 894 (w), 845 (s).

Typical Procedure for Oxidation of Benzyl Alcohols Using Dioxygen Catalyzed by Co(II)DPDPME in the Presence of Isobutylaldehyde

According to the reported procedure, the oxidation of benzyl alcohol was carried out in a 50-mL flask containing benzyl alcohol (1 mmol), Co(II)DPDME (0.01 mmol), acetonitrile (6 mL), and isobutylaldehyde(3 mmol). The reaction mixture was stirred at 60°C for appropriated reaction time. Dioxygen (1 atm) was bubbled through the solution. The reaction was monitored via GC/MS analysis. After completion, the mixture was diluted with diethyl ether and centrifuged to separate the catalyst. Then, the product was analyzed by GC/MS, which can be easily identified by comparing the mass spectra data library.

CONCLUSION

We have demonstrated the utility of the new procedure for the oxidation of alcohols to the carbonyl compounds. This method is efficient and rapid using stoichiometric isobutylaldehyde, environmental dioxygen, and catalytic Co(II)DPDME. Compared with the recently reported methods in which the Cu(II)TPP and Ru(III)TPP have been used as catalysts, the possible mechanism is generally discussed, which provides a new insight into the interaction between metalloporphyrins and dioxygen plus aldehydes. In addition, these studies are useful for our understanding of the natural intermediates involved in metalloporphyrin-catalyzed reaction.

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