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## Oxidation of benzyl alcohols by semi-stoichiometric amounts of cobalt-doped birnessite-type layered MnO<sub>2</sub> under oxygen atmosphere<sup>†</sup>

Akio Kamimura,\*a Yuichiro Nozaki,a Mai Nishiyamab and Masaharu Nakayama\*b

Semi-stoichiometric oxidation of benzylic alcohols to benzaldehydes was readily achieved in heated toluene in the presence of cobalt-doped birnessite MnO<sub>2</sub> under oxygen atmosphere. The oxidation took place selectively for benzylic alcohols, while allylic alcohols were oxidized slowly. No oxidation occurred for usual primary and secondary alcohols. Oxygen atmosphere was important to perform effective oxidation; *i.e.* the oxidation progressed much slower in nitrogen atmosphere. Cobalt-doped birnessite was the best catalyst for the oxidation, in which the amount of birnessite was reduced to 0.7 equivalent of alcohol, resulting in yields of aldehydes greater than 80%. The present method provides a useful green oxidation for benzylic alcohols.

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#### Introduction

Oxidation is one of the most important reactions in organic synthesis.<sup>1</sup> The conversion of primary alcohols to aldehydes is very frequently used in organic transformations. For this purpose, good oxidation reagents/methods have been developed so far. For example, chromium reagents such as PCC<sup>2</sup> and PDC,3 Swern oxidation,4 TPAP,5 Dess-Martin periodinane,6 TEMPO7 and AZADO,8 and MnO29 are typically employed for the conversion of alcohols to aldehydes. Among them, MnO<sub>2</sub> is recognized as a unique oxidation reagent because it achieves selective oxidation for benzylic and allylic alcohols. It is also recognized as a useful reagent because of its wide natural abundance, low-cost, and is environmentally-friendly. However, the oxidation usually requires large excess amounts of MnO<sub>2</sub>. This is a serious drawback for its use in green organic syntheses. Among various MnO<sub>2</sub> polymorphs, birnessite has attracted particular attention owing to its unique catalytic properties.<sup>10</sup> Birnessite has a layered structure composed of edge-shared MnO<sub>6</sub> octahedra containing predominantly Mn<sup>4+</sup> cations as the center ions. Some of the  $Mn^{4+}$  ions are replaced with  $Mn^{3+}$ ions, giving a net negative charge to be compensated by the intercalation of guest cations such as K<sup>+</sup>. We recently found a sufficient activity of readily available birnessite toward oxidation of benzylic and allylic alcohols,<sup>11</sup> where birnessite was prepared by only calcining KMnO<sub>4</sub> and its interlayer was occupied with K<sup>+</sup> ions.<sup>12</sup> However, a large excess amount of birnessite was necessary to achieve efficient oxidation. In the course of our research program in developing new reagents, we were interested in aerobic oxidation using undoped MnO<sub>2</sub> with one-dimensional tunnels.<sup>10g</sup> In this paper, we report a new aerobic oxidation of benzylic alcohols using cobalt-doped birnessite (Co-Bir) that was synthesized according to the solgel procedure.<sup>13</sup> It is generally accepted that the Co ions are located in the MnO<sub>2</sub> frameworks to improve the electrical conductivity of MnO<sub>2</sub>.<sup>14</sup>

#### **Results and discussion**

We first examined the oxidation of benzyl alcohol in the presence of sub-stoichiometric amounts of calcined-birnessite (Scheme 1). The results are summarized in Table 1.

Treatment of **1a** with calcined-birnessite (0.3 g mmol<sup>-1</sup> of **1a**) under nitrogen atmosphere at room temperature did not undergo efficient oxidation; *i.e.* benzaldehyde **2a** was obtained in only 20% yield (entry 1). Use of oxygen atmosphere was also inefficient (entry 2). The oxidation progressed at elevated



Scheme 1 Oxidation of benzyl alcohol 1a by calcinated-birnessite

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<sup>&</sup>lt;sup>a</sup>Department of Applied Molecular Bioscience, Graduate School of Medicine, Yamaguchi University, Ube 75-8611, Japan. E-mail: ak10@yamaguchi-u.ac.jp; Fax: +81 836 85 9231; Tel: +81 836 85 9231

<sup>&</sup>lt;sup>b</sup>Department of Material Chemistry, Graduate School of Science and Engineering, Yamaguchi University, Ube 755-8611, Japan. E-mail: nkymm@yamaguchi-u.ac.jp; Fax: +81 836 85 9201; Tel: +81 836 85 9223

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Table 1 Oxidation of benzyl alcohol 1a under various conditions

Entry	$T/^{\circ}\mathrm{C}$	Atmosphere	<b>2a;</b> Yield (%) <sup><i>a</i></sup>	
1	25	$N_2$	20	
2	25	$O_2$	14	
3	110	$N_2$	70	
4	110	$O_2$	90	
<sup><i>a</i></sup> GC yields				

temperature, giving 2a in 70% yield (entry 3). Benzylalcohol 1a underwent further smooth oxidation when treated with calcined-birnessite under oxygen atmosphere at 110 °C (entry 4), where no over oxidation product was detected. Since this reaction condition seemed promising, we examined various  $MnO_2$  materials under similar conditions (Scheme 2). The results are summarized in Table 2.

Iron-doped birnessite (Fe-Bir) reacted with **1a** to give **2a** in 60% yield (entry 1). The use of Co-Bir improved the yield of **2a** to 89% (entry 2). The doping amount of cobalt affected the efficiency of the oxidation, and the yield of **2a** decreased slightly when Co amount was reduced to 1/10 (entry 3). The similarly-obtained undoped birnessite afforded **2a** in a lower yield (entry 4).

These results suggested that use of Co-Bir achieved effective benzylic oxidation with smaller amounts of the oxidant. Although the reduced amount of  $MnO_2$  led to less efficient oxidation under room temperature conditions, heating to 110 °C under oxygen atmosphere attained sub-stoichiometric oxidation of benzylic alcohols. This procedure was examined for various benzylic alcohols **1** (Scheme 3). The results are summarized in Table 3.

The oxidation progressed smoothly and gave benzaldehyde in good yields. Surprisingly, the amounts of the oxidant could be reduced to 30 mg per 1 mmol of benzyl alcohol without significant loss of the efficiency although a longer reaction time was needed for completion (entry 1). Most of benzyl alcohols were oxidized with 67 to 110 mg per 1 mmol of benzyl alcohol. For example, *o*-methylbenzylalcohol underwent oxidation reaction to afford *o*-tolualdehyde 2b in 81% isolated yield (entry 4). Isolation of the products was quite easily performed; *i.e.* a filtration of the reaction mixture followed by concentration provided the desired aldehyde. The reaction rates for the benzyl alcohols substituted with an electron-donating group were faster than that of the alcohols substituted with an electron-withdrawing group; the oxidation for the latter alcohols required more amounts of Co-Bir (entries 7 and 8).



Scheme 2 Oxidation of benzyl alcohol 1a by MnO2-based oxidant

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Table 2 Oxidation of 1a with various MnO2-based oxidants

Entry	Oxidant	<b>2a</b> ; Yield (%) <sup><i>a</i></sup>	
1	Fe-Bir	60	
2	Co-Bir	89	
3	$\operatorname{Co-Bir}^{b}$	82	
4	Undoped-Bir	71	
<sup><i>a</i></sup> GC yields. <sup><i>b</i></sup> G	One tenth of Co was doped.		

Oxidation for secondary benzylic alcohol was examined (Scheme 4). Phenylethyl alcohol underwent smooth oxidation to give acetophenone **3a** in 87% yield. The reaction rate was almost the same as those observed for benzyl alcohols. On the other hand, the reaction rate decreased as the steric size of R group increased. For example, oxidation of 1-phenyl-2-methyl-1-propanol progressed sluggishly, and only a trace amount of **3c** was observed along with 93% of recovery of the starting alcohol. Thus, the present oxidation procedure is sensitive toward the steric effect from the side chain. For example, treatment of a 1:1 mixture of benzyl alcohol **1a** and phenylpropyl alcohol under the standard reaction conditions under oxygen atmosphere resulted in the selective oxidation of **1a**, and benzaldehyde **2a** and phenylethyl ketone **3b** were obtained in 85% and 3% yields, respectively.

Allylic alcohols were also converted into unsaturated aldehydes, but the reaction rate was much slower than benzylic alcohols (Scheme 5). The reaction was conducted for at least 30 h for these alcohols. For example, cinnamyl alcohol was oxidized to cinnamaldehyde **4a** in 45% yield. A similar treatment gave citral **4b** in 61% yield. Saturated alcohols were not converted to aldehyde **5a** under these conditions and the starting alcohol was recovered.



Scheme 3 Oxidation of benzyl alcohols 1 by cobalt-doped birnessite (Co-Bir)

Table 3 Oxidation of benzylic alcohols with Co-Bir

Entry	R	Time (h)	Oxidant (mg $mmol^{-1}$ )	2;	Yield $(\%)^a$
1	Н	24	30	2a;	$84^b$
2	Н	24	50	2a;	$99^b$
3	Н	4	67	2a;	$89^b$
4	o-Me	6	67	2b;	81
5	<i>p</i> -Me	7	86	2c;	91
6	m-Cl	7	86	2d;	85
7	<i>p</i> -Cl	11	110	2e;	94
8	$p-NO_2$	10	110	2f;	98
9	o-NO <sub>2</sub>	8	86	2g;	85
10	<i>m</i> -MeO	6	86	2h;	90
11	<i>p</i> -Br	7	86	2i;	88

<sup>a</sup> Isolated yields. <sup>b</sup> GC yields.



 $\ensuremath{\mathsf{Scheme}}\xspace 4$  Oxidation of secondary benzylic alcohols 2 and their competitive reaction

As shown in Scheme 6, the competitive oxidation between benzylic and allylic alcohols indicated that the oxidation of benzylic alcohol was much preferred than allylic alcohol. For example a 1 : 1 mixture of benzyl alcohol and 2-cyclohexen-1ol afforded a mixture of benzaldehyde and cyclohexeneone in 54 : 18.

In order to confirm whether the present oxidation had been promoted in the presence of Co-Bir, a leaching test was carried out (Scheme 7). Treatment of benzyl alcohol with a semicatalytic amount of Co-Bir under oxygen atmosphere for 30 min resulted in the formation of benzaldehyde **2a** in 34% yield. The reaction mixture was divided into two; *i.e.* one was supernatant that did not contain Co-Bir catalyst, and the other contained the catalyst. The two mixtures were again exposed to oxygen atmosphere and heated at 110 °C for an additional 5.5 h. The former solution was unchanged and the yield of **2a** was still 34%, while in the latter mixture the reaction progressed and benzyl alcohol was converted to benzaldehyde completely. This clearly shows that the oxidation requires Co-Bir. No oxidation occurred when alcohol was heated under oxygen atmosphere in the absence of Co-Bir.

Considering the amount of Co-Bir, it is reasonable to assume that the oxidation protocol involves catalytic characteristics of  $MnO_2$  because the amount of Co-Bir employed in the reaction was slightly less than the yields of aldehydes. For example, 70 mol% of Co-Bir was used for the oxidation of benzyl alcohol **1a** and benzaldehyde **2a** was obtained in 89% yield (Table 2, entry 3). Thus, the sub-stoichiometric amount of  $MnO_2$  achieved high yields of aldehydes. We assume that



Scheme 6 Competitive reaction between benzyl alcohol and allylic alcohol

the reaction progressed in a similar mechanism to the classical  $MnO_2$  oxidation reaction. The reaction conditions proposed here involve a solid-liquid two-phase heterogeneous process, where the reaction should progress only on the surface of Co-Bir; thereby the actually effective amount of Co-Bir in the reaction should be much smaller than the amount applied. In other words, only a part of Co-Bir would serve as the active oxidant. Even so, this amount of oxidant was at the lower limit for performing effective oxidation, and less amount of oxidant gave moderate to low yields for the aldehydes. Thus, the catalytic performance of  $MnO_2$  is mandatory to achieve such a high yield of aldehyde.

The oxidation activity of birnessite is mainly associated with the presence of Mn<sup>4+</sup>. Therefore, the oxidation of benzyl alcohols proceeds accompanied by the reduction of Mn<sup>4+</sup> sites in the oxide to Mn<sup>3+</sup>. The presence of oxygen can reoxidize the generated Mn<sup>3+</sup> sites back to Mn<sup>4+</sup> that is available for a new oxidation reaction. This view can be thermodynamically supported by the related redox reactions and their standard electrode potentials ( $E^0$ , V vs. SHE), as shown in Scheme 8. Although E<sup>0</sup> values of benzylalcohols were not available in literature, however, as expected from  $E^0$  (-0.197 V) of the ethanol/acetaldehyde couple,15 they are likely sufficiently negative than that (+0.75 V) of MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub>.<sup>16</sup> This means that electrons spontaneously move from alcohol to Mn<sup>4+</sup>. The value (+1.23 V) for the  $O_2/H_2O$  couple is sufficiently positive compared to that (+0.75 V) of MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub>, confirming that the generated  $Mn^{3+}$  ions can be reoxidized to  $Mn^{4+}$  by O<sub>2</sub>. This is probably the reason why the efficient oxidation occurred under oxygen atmosphere in the presence of Co-Bir with substoichiometric amounts. We guess the present catalytic cycle is not very good because the oxidation using less amounts of Co-Bir only afforded aldehydes in poor yields. The turnover number is likely just one or two. Even so the present procedure achieved dramatic reduction of MnO2 for the oxidation of



Scheme 5 Oxidation of allylic alcohols



Scheme 7 Leaching test



 $\label{eq:scheme-sche$ 

benzylic alcohol and it will provide a sustainable method for organic synthesis.

#### Experimental

#### Preparation of Co-doped birnessite (Co-Bir)

Co-doped birnessite (Co-Bir) was prepared by a modified so-gel method according to the literature.<sup>13</sup> A 50 mL of  $CoSO_4$  solution at a concentration of 0.038 or 0.0038 mol L<sup>-1</sup> was mixed to a solution containing 0.028 moles of glucose. The resulting mixture was added quickly to a solution with 0.019 moles of KMnO<sub>4</sub> under vigorous stirring. The molar ratios of Co to Mn were 0.1 and 0.01. The obtained brown gel was cooled at room temperature and then dried at 110 °C overnight. The product was calcined at 400 °C for 2 h, washed thoroughly with water, and then dried at 110 °C overnight.

## Oxidation of benzyl alcohols 1 to benzaldehyde 2; General procedure: Preparation of *o*-tolualdehyde (2b)

A mixture of Co-Bir (67 mg) and *o*-methylbenzylalcohol (122.6 mg, 1.0 mmol) in toluene (10 mL) was heated at 110 °C under oxygen atmosphere for 6 h. The reaction mixture was filtered through celite and concentration of the filtrate gave crude aldehyde, which was purified by Kugelrohl distillation under reduced pressure (170 °C/0.7 mmHg) to give **2b** in 81% yield (97.7 mg). Colorlesss oil; <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 10.28 (1H, s, -CHO), 7.80 (1H, dd, J = 7.8, 1.1 Hz), 7.48 (1H, td, J = 7.5, 1.4 Hz), 7.27 (1H, d, J = 7.6 Hz), 2.68 (3H, s, -CH<sub>3</sub>); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 193.0 (-CHO), 140.7, 134.3, 133.7, 132.1, 131.9, 126.5, 19.6 (-CH<sub>3</sub>).

Other compounds 2 were prepared in a similar manner.

*p*-Tolualdehyde (2c): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.96 (1H, s, -*CHO*), 7.77 (2H, d, *J* = 8.4 Hz), 7.33 (2,H d, *J* = 8.6 Hz), 2.43 (3H, s, -*CH*<sub>3</sub>); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 192.2, 145.7, 134.3, 130.0, 129.8, 21.9 (-CH<sub>3</sub>).

*m*-Chlorobenzaldehyde (2d): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.90 (1H, s, -CHO), 7.77 (1H, t, *J* = 2.0 Hz), 7.68 (1H, dt, *J* = 7.9 Hz, 1.3), 7.52 (1H, dd, *J* = 7.9, 2.8 Hz), 7.41 (1H, t, *J* = 7.8 Hz); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 190.9 (-CHO), 137.9, 135.5, 134.4, 130.4, 129.3, 128.0. *p*-Chlorobenzaldehyde (**2e**): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.98 (1H, s, -*CHO*), 7.82 (2H, dd, *J* = 8.5, 1.9 Hz), 7.51 (2H, dd, *J* = 8.5, 2.1 Hz); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 191.0 (-CHO), 141.1, 134.8, 131.0, 129.6.

*p*-Nitrobenzaldehyde (2**f**): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 10.15 (1H, s, −CHO), 8.39 (2H, d, *J* = 8.7 Hz), 8.07 (2H, d, *J* = 8.8 Hz); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 190.4 (−CHO), 140.1, 130.6, 124.4.

o-Nitrobenzaldehyde (2g): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 10.43 (1H, s, -CHO), 8.12 (1H, dd, *J* = 7.9, 1.2 Hz), 7.96 (1H, dd, *J* = 7.4, 1.8 Hz), 7.85–7.75 (2H, (m); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 188.3 (-CHO), 134.2, 133.8, 131.5, 129.7, 124.6.

*m*-Anisaldehyde (**2h**): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.96 (1H, s, -CHO), 7.47-7.40 (2H, (m), 7.40-7.35 (1H, (m), 7.19-7.13 (1H, (m), 3.84 (3 H, s, -OCH<sub>3</sub>); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 192.3 (-CHO), 160.2, 137.9, 130.1, 123.6, 121.6, 112.1, 55.6 (OCH<sub>3</sub>).

*p*-Bromobenzaldehyde (2i): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.98 (1H, s, -CHO), 7.75 (2H, d, *J* = 8.3 Hz), 7.69 (2H, d, *J* = 8.5 Hz); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 191.2 (-CHO), 135.2, 132.5, 131.0, 129.8.

Acetophenone (3a): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 7.95 (2H, dd, J = 8.3, 1.2 Hz), 7.56 (1H, t, J = 7.4 Hz), 7.46 (2H, t, J = 7.7 Hz), 2.60 (3H, s, PhCOCH<sub>3</sub>); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 198.3 (C=O), 137.2, 133.2, 128.7, 128.4, 26.7 (CH<sub>3</sub>).

Propiophenone (**3b**): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 7.96 (2H, d, J = 7.2 Hz), 7.55 (1H, t, J = 7.4 Hz), 7.45 (2H, t, J = 7.7 Hz), 3.01 (2H, q, J = 7.2 Hz,  $-CH_2CH_3$ ), 1.22 (3H, t, J = 7.2 Hz,  $-CH_2CH_3$ ); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 201.0 (C=O), 137.0, 133.0, 128.7, 128.1, 31.9 (CH<sub>2</sub>), 8.3 (CH<sub>3</sub>).

Cinnamaldehyde (4a): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.70 (1H, d, *J* = 7.7 Hz, -*CHO*), 7.58-7.53 (2H, (m), 7.47 (1H, d, *J* = 16.0 Hz, -CH=CH–), 7.45-7.39 (3H, (m), 6.71 (1H, dd, *J* = 16.0, 7.7 Hz, -CH=CH–); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 193.8 (CHO), 152.9, 134.1, 131.4, 129.2 (C=C), 128.7, 128.6 (C=C).

Citral (**4b**): <sup>1</sup>H NMR  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 9.98 (1H, d, J = 8.1 Hz, -CHO), 5.87 (1H, dd, J = 8.1, 1.1 Hz, =CHCHO), 5.06 (1H, ddd, J = 6.6, 4.0, 1.3 Hz, Me<sub>2</sub>C=CH-), 2.25-2.17 (4H, m, =CHCH<sub>2</sub>CH<sub>2</sub>C(Me)=), 2.16 (3H, s, -C(CH<sub>3</sub>)=CHCHO), 1.68 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C=CH-), 1.60 (3 H, s, (CH<sub>3</sub>)<sub>2</sub>C=CH-); <sup>13</sup>C  $\delta_{\rm C}$  (126 MHz, CDCl<sub>3</sub>): 191.4 (CHO), 164.0 (-C=CHCHO), 133.0(-C=CHCHO), 127.5 (Me<sub>2</sub>C=CH-), 122.6 (Me<sub>2</sub>C=CH-), 40.7 (-C(CH<sub>3</sub>)=CHCHO), 25.8 (-CH<sub>2</sub>CH<sub>2</sub>-), 25.7 (-CH<sub>2</sub>CH<sub>2</sub>-), 17.8 (CH<sub>3</sub>)<sub>2</sub>C=CH-), 17.7 (CH<sub>3</sub>)<sub>2</sub>C=CH-).

#### Conclusions

We have successfully developed a new protocol to oxidize benzylic alcohols using sub-stoichiometric amounts of manganese oxidant. The oxidation progressed smoothly for benzylic alcohols and chemoselectivity is very high. The oxidation is sensitive to steric effects and less hindered alcohols underwent selective oxidation. Use of oxygen atmosphere is important, and the stoichiometry suggests that a catalytic cycle of manganese oxide should be included in the reaction. Indeed, the oxidation potential of manganese oxide and molecular oxygen allows the process to progress thermodynamically. Conventional oxidation procedures using activated  $MnO_2$  require a large excess amount of manganese reagent. On the other hand the present protocol made oxidation possible in sub-stoichiometric amounts of manganese reagents; thus a dramatic reduction of manganese oxidant was achieved. This provides a much greener synthetic process in organic chemistry.

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