Tetrahedron 69 (2013) 5968–5972

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Sub-stoichiometric oxidation of benzylic alcohols with commercially available activated MnO_2 under oxygen atmosphere: a green modification of the benzylic oxidation

Akio Kamimura *, Hiroyuki Komatsu, Takaaki Moriyama, Yuichiro Nozaki

Department of Applied Molecular Bioscience, Graduate School of Medicine, Yamaguchi University, Ube 755-8611, Japan

ARTICLE INFO

Article history:
Received 26 March 2013
Received in revised form 19 April 2013
Accepted 21 April 2013
Available online 6 May 2013

Keywords:
Manganese oxide
Benzylic oxidation
Green oxidation
Aerobic oxidation

ABSTRACT

Benzylic and allylic alcohols were readily converted into aldehydes and ketones in the presence of sub-stoichiometric amounts of activated MnO_2 under oxygen atmosphere. No over-oxidation to carboxylic acid happened. The present procedure dramatically reduces the amounts of MnO_2 necessary for the oxidation and provides a greener modification of widely used oxidation method.

1. Introduction

Oxidation of alcohols to aldehydes or ketones is an important transformation in organic synthesis.[1] Use of various oxidation methods, such as PCC or PDC oxidation,[2] Swern oxidation,[3] TPAP oxidation,[4] Dess-Martin periodate,[5] TEMPO[6] and AZADO,[7] and MnO_2 based oxidation reaction,[8] are currently used widely for organic synthesis. Among of these methods, MnO_2 oxidation occupies a unique position because it selectively oxidizes benzylic and allylic alcohols to the corresponding aldehydes and ketones. Although it provides a simple reaction procedure, MnO_2 should be activated beforehand; so far several activation methods are known, such as Attenborough method. Instead of these methods, commercially available activated MnO_2[9] has been recently used as a convenient oxidant. Another drawback of the reaction is that it requires a large excess amount of MnO_2 reagents, a heavy metallic reagent, for achieving the sufficient oxidation results. Recently we have developed birnessite MnO_2[10] as a new reagent for the oxidation.[11] We reported that cobalt-doped birnessite MnO_2 under oxygen atmosphere achieved dramatic reduction of the amounts of the oxidant; the oxidation of benzylic and allylic alcohols was achieved using only the sub-stoichiometric amounts of the manganese oxidant.[12] The necessary amounts of the manganese reagents reached 1/30 to 1/40 comparing with the conventional MnO_2 oxidation; 1 equiv or less amounts of the oxidant gave good results. During the course of our research, we thought that commercially available activated MnO_2 might perform the oxidation under similar reaction conditions, and such modification would provide a much greener method to organic synthesis. In this paper we show reduced amounts of activated MnO_2 also serves as a good oxidation reagents for benzylic and allylic alcohols. A dramatic reduction of the amounts of manganese oxide for the oxidation is demonstrated.

2. Results and discussion

We first examined various conditions for the oxidation of benzhydrol **1**. The results are summarized in Table 1.

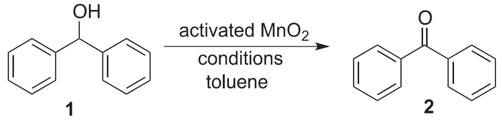
Benzhydrol **1** was readily oxidized under conventional reaction conditions employing large excess amounts of MnO_2, and benzophenone **2** was isolated in quantitative yield (entry 1). Use of reduce amounts of MnO_2, however, failed the smooth oxidation and compound **2** was detected only 7% (entry 2). This was almost the same for the reaction performed under oxygen atmosphere (entry 3). Heating of the reaction mixture improved the yield of **2** to 60% under nitrogen atmosphere (entry 4). Benzophenone **2** was obtained in quantitative yield when compound **1** was treated with sub-stoichiometric amounts of MnO_2 at 110 °C in toluene under air or oxygen atmosphere (entry 5 and 6). The amounts of MnO_2 were reduced to 50 mg/mmol without loss of the yields of **2** (entry 7),

---

* Corresponding author. Tel.: +81 836 85 9231; fax: +81 836 85 9201; e-mail address: ak10@yamaguchi-u.ac.jp (A. Kamimura).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.04.109

Table 1
Oxidation of benzhydrol **1** under various conditions



Entry	Amounts of MnO_2 (mg/mmol)	Atmosphere	Time (h)	Temp (°C)	**2**; Yield (%)[a]
1	1750	N_2	3	25	53
2	100	N_2	3	25	7
3	100	O_2	3	25	8
4	100	N_2	3	110	60
5	100	Air	3	110	98
6	100	O_2	3	110	100
7	50	O_2	8	110	98
8	30	O_2	8	110	65
9	10	O_2	8	110	42

[a] Isolated yield.

while the yield decreased very much when 30 or 10 mg/mmol of MnO_2 was employed (entry 8 and 9).

We next examined these conditions for the oxidation of benzyl alcohol **3a**. The results are summarized in Table 2.

Table 2
Oxidation of benzyl alcohols **3a** to benzaldehydes **4**

$$\underset{\mathbf{3a}}{PhCH_2OH} \xrightarrow[\text{toluene/4h}]{MnO_2\ (70\ mg/mmol)} \underset{\mathbf{4a}}{PhCHO}$$

Entry	Temp (°C)	Atmosphere	**4a**; Yield (%)[a]
1	25	N_2	2
2	25	O_2	3
3	110	N_2	32
4	110	Air	42
5	110	O_2	85

[a] GC yield.

As expected, almost no oxidation occurred in the reaction at room temperature (entry 1 and 2). Benzaldehyde **4a** was obtained in 32% yield by the reaction under heating conditions under nitrogen atmosphere (entry 3). The yield of **4a** was slightly improved under air atmosphere (entry 4). Satisfactory yield of **4a** was finally obtained by the oxidation under oxygen atmosphere (entry 5).

With the optimized conditions in hand, we examined the present reaction conditions for the oxidation of various types of benzyl alcohols **3**. The results are summarized in Table 3.

Anisalcohol **3b** was smoothly oxidized to give anisaldehyde **4b** in 93% yield (entry 1). No over oxidation to benzoic acid was observed under the present reaction conditions. The reaction completed in 8 h. Isolation work was readily achieved by the filtration followed by concentration. Occasionally chromatographic purification was necessary for obtaining pure aldehydes **4**. Some benzyl alcohols that have an electron withdrawing substituents underwent slow oxidation and the reaction requires slightly more amounts of MnO_2 to give corresponding aldehydes **4** in lower reactivity and in moderate yields (entries 2, 5, and 9). Sterically demanded alcohol, such as 2,6-dicholorobenzyl alcohol gave the aldehyde **4l** in low yield (entry 11). Heteroaromatic alcohols also gave corresponding aldehydes, but due to its volatility the isolated yield remained in moderate level (entry 6).

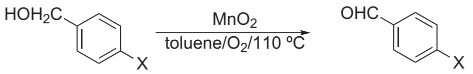
We used **3h** and **3k** to examine necessary amounts of MnO_2 for completion of the reaction (Scheme 1). In both cases, 70 mg/mmol was the optimized amounts for the oxidation, and use of less amounts of MnO_2 gave **4h** and **4k** in moderate to low yields.

Table 3
Oxidation of benzylic alcohols **3** to aldehydes **4**

$$\underset{\mathbf{3}}{ArCH_2OH} \xrightarrow[\substack{\text{toluene}/O_2/110\ ^\circ C \\ 8\ h}]{MnO_2} \underset{\mathbf{4}}{ArCHO}$$

Entry	Ar	MnO_2 (g/mmol)	**4**; Yield (%)[a]
1	4-MeO	50	**4b**; 93
2	3-MeO	100	**4c**; 93[c]
3	3,4-$(OCH_2O)C_6H_3$	50	**4d**; 84
4	3,4-$(MeO)_2C_6H_3$	70	**4e**; 99
5	2-Naphthyl	100	**4f**; 89
6	2-Furyl	70	**4g**; 34 (23)[b]
7	4-$NO_2C_6H_4$	70	**4h**; 89
8	2-$NO_2C_6H_4$	70	**4i**; 75
9	4-ClC_6H_4	100	**4j**; 64
10	4-BrC_6H_4	70	**4k**; 74
11	2,6-$Cl_2C_6H_3$	100	**4l**; 29
12	3-BrC_6H_4	70	**4m**; 61
13	4-MeC_6H_4	70	**4n**; 90
14	3-MeC_6H_4	70	**4o**; 66
15	2-MeC_6H_4	70	**4p**; 85

[a] Isolated yield.
[b] Recovery of starting benzylic alcohol **3**.
[c] Use of 70 mg/mmol of MnO_2 gave **4c** in 54%.



3h; X = NO_2
3k; X = Br

4h; 32% (10 mg/mmol) 62% (30 mg/mmol) 72% (50 mg/mmol) 89% (70 mg/mmol)	**4k**; 23% (10 mg/mmol) 54% (30 mg/mmol) 61% (50 mg/mmol) 74% (70 mg/mmol)

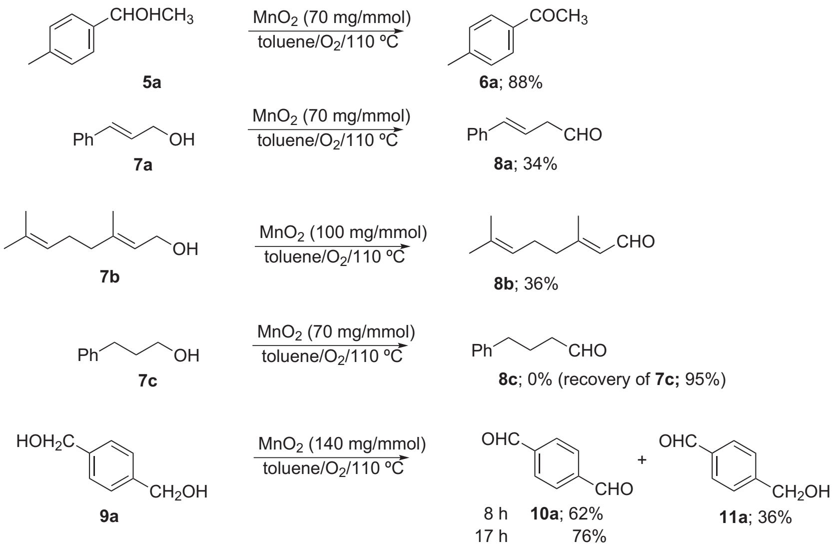
Scheme 1. Oxidation of **3h** and **3k** with various amounts of MnO_2.

The present reaction conditions were useful for the other substrates (Scheme 2). For example, *p*-methylphenylethyl alcohol **5a** was readily oxidized to give acetophenone **6a** in 88% yields. Cinnamyl alcohol underwent slow oxidation, giving cinnamaldehyde **8a** in 34% yield. Other allylic alcohol **7b** also gave unsaturated aldehyde **8b** in poor yield. Saturated aliphatic alcohol **7c** was inert toward the present reaction conditions and compound **7c** was recovered in 95% yield. Double oxidation smoothly occurred when benzyldiol **9a** was used for the reaction, but slightly more amounts of MnO_2 were required and mono-oxidized products **11a** were obtained as a side product. The yield of **10a** was improved to 76% when the diol was exposed to the reaction mixture for 17 h.

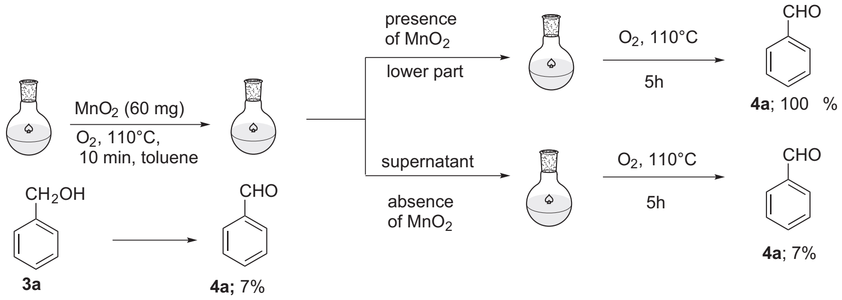
The present oxidation happens when MnO_2 was employed under oxygen atmosphere. Use of oxygen atmosphere in the absence of MnO_2 did not promote the oxidation reaction. Thus, benzaldehyde **3a** was treated under O_2 atmosphere in the presence of MnO_2 for 10 min. Then the reaction mixture was divided into two, one contained MnO_2 and the other was supernatant without MnO_2. The two reaction flasks were again maintained under O_2 atmosphere and heated to 110 °C for additional 5 h. The flask containing MnO_2 gave benzaldehyde **4a** in quantitative yield, while the yield of **4a** was unchanged for the supernatant solution. These results clearly show that the oxidation occurs only in the presence of MnO_2 and O_2 was not the direct oxidant for **3a** (Scheme 3).

The amounts of MnO_2 were slightly less than the yield of aldehydes so that partial re-oxidation of MnO_2 should occur, and there is a possibility of a catalytic cycle of MnO_2 could exist. However, the catalytic cycle should be very inefficient so that sub-stoichiometric amounts of MnO_2 were required for obtaining satisfactory yield of aldehydes. We examined reuse of the MnO_2 for the oxidation of **1a**, but the oxidation did not complete to give **2a** in 42% for the second time, 24% for the third time, and 16% for the fourth time (Scheme 4).

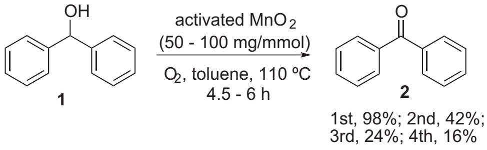
In conclusion, we have successfully developed a new method for the oxidation of benzylic alcohols in sub-stoichiometric amounts of MnO_2. The activated MnO_2 used here is normally commercially



Scheme 2. Oxidation of secondary benzyl alcohol and allylic alcohols.



Scheme 3. Oxidation in the presence or absence of MnO_2.



Scheme 4. Recycling use of MnO_2.

available. Present modification dramatically reduced the necessary amounts of MnO_2 for the smooth oxidation. The reduction reached almost 1/30 of the conventional method. We hope the present methods will contribute a green transformation reaction in organic synthesis.

3. Experimental section

Caution: The present conditions may have a risk of fire although it has never happened in our whole experimental works.

3.1. Oxidation of benzhydrol 1a in the presence of sub-stoichiometric amounts of activated MnO$_2$: preparation of benzophenone 2 (Table 1, entry 6). General procedure

Benzhydrol **1** (0.3831 g, 2.08 mmol) was dissolved in toluene (15 mL) and activated MnO_2 (purchased from Aldrich, 0.106 g, 1.92 mmol, 50 mg/mmol) was added to the solution. The reaction mixture was heated at 110 °C under oxygen atmosphere for 4 h. Supernatant of the reaction mixture was scooped by pipet. Additional toluene (5 mL) was added to solid residue and washed the solid then the supernatant was scooped by pipet. This washing procedure was repeated for four times. All of toluene solution was combined and concentrated. Crude product was purified by flash chromatography (silica gel/hexane–EtOAc 3:1) to give **2** in 98% yield (0.373 g, 2.05 mmol). MnO_2 residue was examined for the recycling use of the oxidant (Scheme 4, see below). White solid; mp 47–48 °C (lit. 47–51 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J=8.2, 1.2 Hz, 4H), 7.59 (dd, J=10.6, 4.3 Hz, 2H), 7.48 (dd, J=10.8, 4.8 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 137.7 (2C), 132.5 (2C), 130.2 (4C), 128.4 (4C).

Other benzaldehydes **4** were prepared in a similar manner.

*3.1.1. p-Anisaldehyde (**4b**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.84 (d, J=8.9 Hz, 2H), 7.00 (d, J=8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 164.7, 132.1 (2C), 130.0, 114.4 (2C), 55.7.

*3.1.2. m-Anisaldehyde (**4c**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.48–7.41 (m, 2H), 7.39 (d, J=2.4 Hz, 1H), 7.18 (dt, J=6.6, 2.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 160.2, 137.9, 130.2, 123.8, 121.7, 112.0, 55.6.

*3.1.3. Piperonal (**4d**).* White solid; mp 34.5–35 °C (lit. 35–39 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.41 (dd, J=7.9, 1.6 Hz, 1H), 7.33 (d, J=1.5 Hz, 1H), 6.93 (d, J=7.9 Hz, 1H), 6.07 (s, 2H), 1.57 (s, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 153.2, 148.8, 132.0, 128.9, 108.5, 107.0, 102.2.

*3.1.4. 3,4-Dimethoxybenzaldehyde (**4e**).* White solid; mp 41.5–42.5 °C (lit. 40–43 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.46 (dd, *J*=8.2, 1.9 Hz, 1H), 7.41 (d, *J*=1.8 Hz, 1H), 6.98 (d, *J*=8.2 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 154.6, 149.7, 130.2, 127.1, 110.4, 108.9, 56.3, 56.1.

*3.1.5. 2-Naphthaldehyde (**4f**).* White solid; mp 58–59 °C (lit. 58–61 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.35 (d, *J*=0.5 Hz, 1H), 8.01 (dd, *J*=8.2, 0.5 Hz, 1H), 7.96 (dd, *J*=8.5, 1.5 Hz, 1H), 7.94 (d, *J*=8.5 Hz, 1H), 7.91 (d, *J*=8.3 Hz, 1H), 7.65 (ddd, *J*=8.2, 6.9, 1.3 Hz, 1H), 7.59 (ddd, *J*=8.1, 6.9, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 136.6, 134.8, 134.2, 132.7, 129.6, 129.3, 129.2, 128.2, 127.2, 122.9.

*3.1.6. 2-Furfural (**4g**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.90–7.55 (m, 1H), 7.25 (dd, *J*=3.6, 1.4 Hz, 1H), 6.60 (dt, *J*=3.4, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 153.0, 148.2, 121.2, 112.7.

*3.1.7. 4-Nitrobenzaldehyde (**4h**).* Pale yellow solid; mp 102.5–103 °C (lit. 103–106 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.40 (d, *J*=8.5 Hz, 2H), 8.07 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 151.2, 140.1, 130.6 (2C), 124.4 (2C).

*3.1.8. 2-Nitrobenzaldehyde (**4i**).* Pale yellow solid; mp 41–42 °C (lit. 42–44 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.12 (d, *J*=7.9 Hz, 1H), 7.96 (d, *J*=7.4 Hz, 1H), 7.80 (t, *J*=7.4 Hz, 1H), 7.76 (t, *J*=7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.3, 134.2, 133.8, 131.5, 129.8, 124.6.

*3.1.9. 4-Chlorobenzaldehyde (**4j**).* White solid; mp 44.5–45 °C (lit. 45–50 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, *J*=8.3 Hz, 2H), 7.52 (d, *J*=8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 141.1, 134.8, 131.0 (2C), 129.6 (2C).

*3.1.10. 4-Bromobenzaldehyde (**4k**).* White solid; mp 55–56 °C (lit. 55–58 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.75 (d, *J*=8.3 Hz, 2H), 7.69 (d, *J*=8.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 135.1, 132.6 (2C), 131.1 (2C), 129.9.

*3.1.11. 2,6-Dichlorobenzaldehyde (**4l**).* White solid; mp 67–68 °C (lit. 69–71 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.34 (s, 2H), 7.21 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 137.0, 133.7 (2C), 130.5, 129.9 (2C).

*3.1.12. 3-Bromobenzaldehyde (**4m**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.01 (s, 1H), 7.81 (d, *J*=7.6 Hz, 1H), 7.75 (ddt, *J*=8.0, 1.8, 0.8 Hz, 1H), 7.42 (t, *J*=7.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 138.1, 137.4, 132.5, 130.7, 128.5, 123.5.

*3.1.13. 4-Tolualdehyde (**4n**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.77 (d, *J*=7.9 Hz, 2H), 7.32 (d, *J*=7.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 145.7, 134.3, 130.0 (2C), 129.8 (2C), 22.0.

*3.1.14. 3-Tolualdehyde (**4o**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.72–7.61 (m, 2H), 7.47–7.33 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 139.0, 136.5, 135.4, 130.1, 129.0, 127.3, 21.3.

*3.1.15. 2-Tolualdehyde (**4p**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.80 (dd, *J*=7.6, 1.3 Hz, 1H), 7.47 (td, *J*=7.5, 1.4 Hz, 1H), 7.36 (t, *J*=7.5 Hz, 1H), 7.26 (d, *J*=7.0 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 140.7, 134.2, 133.8, 132.2, 131.9, 126.4, 19.7.

*3.1.16. 4-Methylacetophenone (**6**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J*=8.2 Hz, 2H), 7.25 (d, *J*=8.6 Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 144.0, 134.8, 129.3 (2C), 128.5 (2C), 26.6, 21.7.

*3.1.17. Cinnamaldehyde (**8a**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, *J*=8.1 Hz, 1H), 7.62–7.51 (m, 2H), 7.47 (dd, *J*=16.1, 1.5 Hz, 1H), 7.47–7.34 (m, 3H), 6.71 (ddd, *J*=15.8, 7.6, 0.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 153.0, 134.1, 131.4, 129.2, 128.7, 128.6.

*3.1.18. Citroneral (**8b**).* Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 9.98 (d, *J*=8.2 Hz, 1H), 5.87 (d, *J*=8.1 Hz, 1H), 5.11–5.01 (m, 1H), 2.25–2.17 (m, 4H), 2.16 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 164.1, 133.1, 127.5, 122.6, 40.7, 25.8, 25.7, 17.9, 17.7.

*3.1.19. Terephthalaldehyde (**10a**).* White solid; mp 112–113 °C (lit. 114–116 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 2H), 8.05 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6 (2C), 140.1 (2C), 130.3 (2C).

3.2. Procedure for leaching test (Scheme 3)

A mixture of benzyl alcohol **3a** (0.1195 g, 1.105 mmol), tridecane (internal standard, 0.1971 g, 1.069 mmol) and MnO_2 (59.8 mg, 0.68 mmol) in toluene (10 mL) was heated at 110 °C under oxygen atmosphere for 10 min. GC analysis revealed the yield of benzaldehyde **4a** was 7%. The reaction mixture was divided into two, one was supernatant, and the other was the reaction mixture containing MnO_2. The two reaction mixture were heated at 110 °C under oxygen atmosphere for additional 5 h. GC analyses indicated the yields of **4a** were 7% for the former solution and 100% for the latter mixture.

3.3. Recycling use of MnO_2 (Scheme 4), second time and later

A mixture of **1** (0.365 g, 1.98 mmol) and MnO_2 (recovered from the reaction of **1**, see above) in toluene (10 mL) was heated at 110 °C under oxygen atmosphere for 6 h. Supernatant of the reaction mixture was separated and MnO_2 residue was washed with toluene for three times. The supernatant and the wash solution were combined and evaporated. Crude product was purified through flash chromatography (silica gel/hexane–EtOAc 3:1) to give **2** in 42% yield (0.150 g, 0.82 mmol). The third time use was examined from **1** (0.343 g, 1.876 mmol) and **2** was isolated in 24% yield (0.080 g, 0.44 mmol). The fourth time use was examined from **1** (0.311 g, 1.69 mmol) and **2** was isolated in 16% yield (0.048 g, 0.263 mmol).

Supplementary data

Spectroscopic charts for compounds **2**, **4**, **6**, **8**, and **10**. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.109.

References and notes

1. *Handbook of Reagents for Organic Synthesis, Oxidizing and Reducing Agents*; Burke, S. D., Danheiser, R. L., Eds.; John Wiley and Sons: Chichester, UK, 1999.
2. (a) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647; (b) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *20*, 399.
3. Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
4. (a) Griffith, W. P.; Ley, S. V. *Aldrichimica Acta* **1990**, *23*, 13; (b) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.
5. (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155; (b) Boeckman, R. K., Jr.; Shao, P.; Mullins, J. J. *Org. Synth.* **2000**, *77*, 141.

6. (a) Vogler, T.; Studer, A. *Synthesis* **2008**, 1979; (b) Piancatelli, G.; Leonelli, F. *Org. Synth.* **2006**, *83*, 18 and references cited therein.
7. (a) Shibuya, M.; Tomizawa, M.; Suzuki, I.; Iwabuchi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 8412; (b) Shibuya, M.; Sato, T.; Tomizawa, M.; Iwabuchi, Y. *Chem. Commun.* **2009**, 1739; (c) Tomizawa, M.; Shibuya, M.; Iwabuchi, Y. *Org. Lett.* **2009**, *11*, 1829; (d) Shibuya, M.; Sasano, Y.; Tomizawa, M.; Hamada, T.; Kozawa, M.; Nagahama, N.; Iwabuchi, Y. *Synthesis* **2011**, 3418; (e) Shibuya, M.; Osada, Y.; Sasano, Y.; Tomizawa, M.; Iwabuchi, Y. *J. Am. Chem. Soc.* **2011**, *133*, 6497.
8. (a) Fatiadi, A. J. *Synthesis* **1976**, 65; (b) Fatiadi, A. J. *Synthesis* **1976**, 133; (c) Attenburrow, J.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094; (d) Mancera, O.; Rosenkranz, G.; Sondheimer, F. *J. Chem. Soc.* **1954**, 3271; (e) Mattock, A. R. *J. Chem. Res., Synop.* **1977**, 40; (f) Harfenist, M.; Bavley, A.; Lazier, W. A. *J. Org. Chem.* **1954**, *19*, 1608; (g) Ball, S.; Goodwin, T. W.; Morton, R. A. *Biochem. J.* **1948**, *42*, 516; (h) Carpino, L. A. *J. Org. Chem.* **1970**, *35*, 3971; (i) Goldman, I. M. *J. Org. Chem.* **1969**, *34*, 1979; (j) Belew, J. S.; Tek-Ling, C. *Chem. Ind. (London)* **1967**, 1958; (k) Fatiadi, A. J. *J. Chem. Soc. B* **1971**, 889.
9. Activated MnO_2 is available from Sigma–Aldrich.
10. (a) Luo, J.; Huang, A.; Park, S. H.; Suib, S. L.; Young, C.-L. O. *Chem. Mater.* **1998**, *10*, 1561; (b) Pietro, O.; Del Arco, M.; Rives, V. *J. Mater. Sci.* **2003**, *38*, 2815; (c) Cai, J.; Suib, S. L. *Inorg. Chem. Commun.* **2001**, *4*, 493; (d) Frias, D.; Nousir, S.; Barrio, I.; Montes, M.; Centeno, M. A.; Odriozola, J. A. *Mater. Charact.* **2007**, *58*, 776; (e) Yang, L.-X.; Zhu, Y.-J.; Cheng, G.-F. *Mater. Res. Bull.* **2007**, *42*, 159; (f) Morales, J.; Sanchez, L.; Bach, S.; Pereira-Ramos, J. P. *Mater. Lett.* **2002**, *56*, 653; (g) Son, Y.-C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4280.
11. Kamimura, A.; Nozaki, Y.; Ishikawa, S.; Inoue, R.; Nakayama, M. *Tetrahedron Lett.* **2011**, *52*, 538.
12. Kamimura, A.; Nozaki, Y.; Nishiyama, M.; Nakayama, M. *RSC Adv.* **2013**, *3*, 468.