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K-birnessite MnO_2: a new selective oxidant for benzylic and allylic alcohols

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ABSTRACT

K-birnessite, which is readily prepared by the pyrolysis of $KMnO_4$, acts as a convenient new oxidant for benzylic and allylic alcohols.

Selective oxidation of alcohols to aldehydes is an important transformation in organic synthesis. A number of useful methods have been developed for the oxidation so far. For example, the use of chromium oxide, such as pyridinium chlorochromate (PCC)[1] and pyridiunium dichromate (PDC),[2] and Swern oxidation[3] are typical strategies for the selective preparation of aldehydes from primary alcohols. Tetrapropylammonium perruthenate (TPAP)[4] and Dess–Martin periodinane (DMP)[5] are improved oxidants for mild oxidation of alcohols. Recently some methods for aerobic oxidation of alcohol by using gold cluster are reported.[6]

Among these oxidants, manganese oxide (MnO_2) is a unique class of oxidant owing to its capability to achieve selective and mild oxidation of benzylic and allylic alcohols.[7] For the oxidation, MnO_2 must be activated prior to use. Among the various activation methods developed to date,[8] Attenburrow's method[8a] is the representative one, in which $KMnO_4$ and $MnSO_4$ are treated in alkaline solution and the precipitate is dried at 120 °C. The efficiency of the oxidant depends on the activation processes of MnO_2 which requires special care for the treatment. For example, the water content of MnO_2 critically affects the efficiency of the oxidation, that is completely dried MnO_2 is useless for the oxidation. The activated MnO_2 materials consist of an amorphous structure.[9] Recently, an interesting modification of aerobic oxidation by using catalytic amounts of K-OMS was reported.[10] Although several modern methods are devised recently, MnO_2 oxidation is still the most reliable and controllable method in organic synthesis for the conversion of benzylic and allylic alcohols into the corresponding aldehydes.

Birnessite, also called as δ-type MnO_2, has a two-dimensional layered structure with an interlayer distance of ~0.7 nm, and is comprised of edge-sharing MnO_6 octahedra. Small cations such as potassium ions or protons are located in the interlayer space to balance the negative charges on manganese oxide layers. In such a layered structure, all of the material can be regarded as a surface. This is different from bulk materials, in which not all of metal ions can be involved in the electron-transfer reactions. Birnessites have been synthesized by a wide variety of chemical methods, including oxidation of Mn^{2+} cations,[11] reduction of $KMnO_4$,[12] and high-temperature decomposition of $KMnO_4$.[13] However, very few studies report the electrochemical synthesis of birnessite as a thin film.[14] Thermolysis of $KMnO_4$ is the simplest method to obtain highly-crystallized birnessite, which may offer a peculiar oxidation reactivity owing to its unique nanolayered structure. To the best of our knowledge, however, no studies have been reported on the use of birnessite in organic synthesis. In this paper, we report a new selective oxidation of benzylic and allylic alcohols by birnessite-type MnO_2 intercalated with potassium ions (K-birnessite), that is very easily prepared by heat-treatment of commercially available $KMnO_4$.

K-birnessite was prepared by the reported method.[13] $KMnO_4$ was gradually heated in air to 800 °C over 13 h, then maintained at that temperature for an additional 5 h. The crude K-birnessite was cooled and washed thoroughly with water to remove the remaining $KMnO_4$. After that the product was dried at 80 °C overnight. Peaks at 12.5° and 25.1° in 2θ can be indexed to the 001 plane and its second (002) order diffractions from multilayers of birnessite-type manganese oxide (Fig. 1).[15] *d*-spacing of the 001 peak (*d*001) corresponds to the interlayer spacing and was measured to be 0.71 nm according to Bragg's equation. Four small peaks appearing between 36.4° and 44.6° are associated with the intrasheet reflections,[16] indicating that each manganese oxide sheet is crystallized. All the above features are consistent with those generally observed for K-birnessite. The full width at half-maximum of the 001 peak was measured to be 0.173°, corresponding to a crystallite size of 22 nm in the 001 direction, deduced by the Scherrer equation ($k = 0.89$). Thus, there is no doubt that we used highly-crystallized birnessite as the catalyst.

Oxidation by K-birnessite was carried out in the following procedure. K-birnessite was added to a solution of alcohol **1** (1 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting suspension was stirred for 2 h. After filtration of the mixture, the crude aldehyde or ketone **2** was isolated by concentration of the filtrate. The results are summarized in Table 1.

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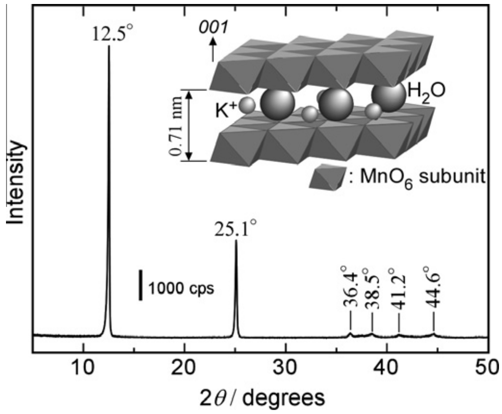
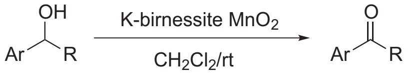


Figure 1. XRD pattern of K-birnessite.

Table 1
Oxidation of benzyl alcohol by K-birnessite



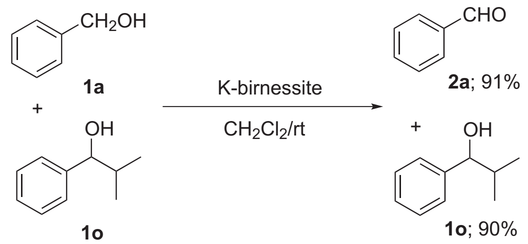
1; 1 mmol **2**

Entry	Ar	R	Amounts (g/mmol)	Time (h)	**2**; yield[a] (%)
1	Ph	H	0.45	2	**2a**; 20[b]
2	Ph	H	1.73	2	**2a**; 59[b]
3	Ph	H	3.03	2	**2a**; 89
4	*m*-ClC_6H_4	H	2.86	3	**2b**; 88
5	*p*-ClC_6H_4	H	2.95	7	**2c**; 90
6	*p*-$O_2NC_6H_4$	H	2.92	10	**2d**; 85
7	*o*-$O_2NC_6H_4$	H	2.99	4.5	**2e**; 78
8	*m*-$O_2NC_6H_4$	H	3.00	4	**2f**; 80
9	*p*-$MeOC_6H_4$	H	2.68	3	**2g**; 99
10	*m*-$MeOC_6H_4$	H	2.91	3	**2h**; 67
11	*o*-MeC_6H_4	H	3.03	2	**2i**; 71
12	*p*-BrC_6H_4	H	3.03	7	**2j**; 86
13	2-Furanyl	H	3.00	2	**2k**; 85
14	2-Thienyl	H	3.00	2	**2l**; 82
15	Ph	Me	3.00	2	**2m**; 89
16	Ph	Et	3.03	3	**2n**; 79
17	Ph	^{i}Pr	2.86	9	**2o**; 70[c]

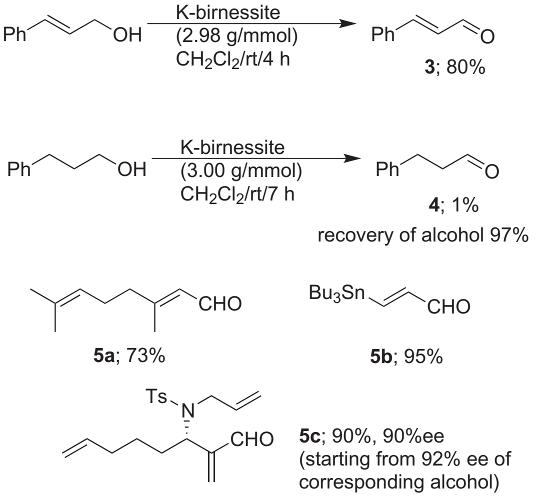
[a] Isolated yield.

[b] GC yield.

[c] The yield of **2o** was 0% when treated with commercially available activated MnO_2 for 9 h.



Scheme 1.



Scheme 2.

The reaction occurred smoothly and desired benzaldehyde (**2a**) was detected by GC analysis. Benzyl alcohol was consumed within 2 h when 0.45 g/mmol of K-birnessite was used, and the amounts of benzaldehyde (**2a**) gradually increased. However, the reaction stopped when the yield of **2a** reached about 20% (entry 1). We thought this was due to insufficient amounts of K-birnessite to complete the reaction so we increased the amounts of K-birnessite (entries 2 and 3). The yield of **2a** was improved to about 89% when 3 g/mmol of K-birnessite was used for the oxidation (entry 3). The necessary amount of manganese oxide is almost similar to that of commercially available activated MnO_2 to progress the practical oxidation reaction.

With the optimized reaction conditions in hand, we examined the oxidation of other benzyl alcohol derivatives. The oxidation took place smoothly in 2 h and corresponding benzaldehyde **2** was isolated in good yield. The isolation procedure was simple; just filtration and concentration gave aldehyde in good yield.[17] Some alcohols required longer reaction time. For example, chloro- and nitro-substituted benzyl alcohols were oxidized more slowly and consumed 4–10 h until the completion of the reaction (entries 5–8, 12), while the yields of the aldehydes **2** were almost equally high. Heteroaromatic compounds also underwent the smooth oxidation to give corresponding aldehydes in good yield (entries 13 and 14). Thus, the present oxidation was compatible to these functional groups.

The present method is useful for the oxidation of secondary alcohols to give ketones (entries 15–17). For example, treatment of α-phenethyl alcohol (**1m**) with K-birnessite resulted in the formation of acetophenone (**2m**) in 89% yield. Propiophenone (**2n**) was also prepared from the corresponding alcohol, but the sterically demanded alcohol required longer reaction time to give ketones in good yield. It should be noted that the present reaction rate was much faster than the commercially available MnO_2 which could not oxidize 2-methyl-1-phenyl-1-propanol (**1o**) after 9 h of treatment. Comparing with the oxidation of primary alcohol, the reaction rate for the secondary alcohol was remarkably slow. For example, a competitive reaction between benzyl alcohol (**1a**) and α-phenylethyl alcohol (**1m**) showed that the reaction rate of the primary alcohol was about six times faster than the secondary alcohol. It should be noted that selective oxidation of benzyl alcohol was achieved from a mixture of benzyl alcohol (**1a**) and 2-methyl-1phyenyl-1-propanol (**1o**) (Scheme 1).

The present oxidative reagent is also effective toward the selective oxidation of allylic alcohol. For example, cinnamyl alcohol readily gave cinnamaldehyde (**3**) in 80% yield (Scheme 2). It should be mentioned that 3-phenyl-1-propanol, saturated derivative of cinnamyl alcohol, was inert under the present reaction conditions and the corresponding aldehyde **4** was detected only 1% after 7 h of the reaction time; the starting alcohol was recovered in 97%. Other allylic alcohols were successfully oxidized to give the corresponding unsaturated aldehydes **5**. For example, geraniol gave citral (**5a**) in 73% yield. Stanny allylic alcohol was also converted into stannyl unsaturated aldehyde **5b**[18] in 95% yield. Chiral alcohol underwent smooth oxidation within 3 h and gave unsaturated aldehyde **5c** in 90% yield.[19] The reaction occurred in a spot-to-spot manner and purification of **5c** was quite easy. It should be noted that no significant racemization at C3 chiral center was observed during the reaction. Although the same oxidation was achieved by using commercially available activated MnO_2 under similar conditions (abt 3 g/mmol), it took more than 10 h until the completion of the reaction. The yield of **5c** was only 70% along with the formation of small amounts of side products, and the purification of **5c** was not very easy. Thus, this birnessite is a much superior oxidant to commercially available MnO_2 for the preparation of α,β-unsaturated aldehydes.

In conclusion, we have developed a new oxidizing reagent for allylic and benzylic alcohols. K-birnessite is readily prepared from commercially available $KMnO_4$ by the thermal treatment at 800 °C in a readily available electric muffle furnace. This is the first oxidizing reagent in crystalline state of MnO_2. Optimum molar ratio for the reaction is about 3 g of K-birnessite per 1 mmol of alcohol. Neither oxidation of aliphatic primary alcohol nor over-oxidation to carboxylic acid was observed under the present conditions. Thus, use of K-birnessite will provide a useful oxidizing method in organic synthesis.

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17. *Oxidation of p-chlorobenzyl alcohol (*Table 1*, entry 5). Typical procedure*: To a solution of *p*-chlorobenzyl alcohol (143.4 mg, 1.01 mmol) in CH_2Cl_2 (10 mL) was added K-birnessite (2.98 g). The reaction mixture was stirred at 30 °C for 7 h. Black precipitate was removed by filtration over celite. The filtrate was concentrated to give crude *p*-benzaldehyde, which was purified through flash chromatography (silica gel/hexane–EtOAc) to give **2c** in 90% yield (129.1 mg).
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19. *Preparation of (S)-3-(N-allyl-N-tosyl)amino-2-methylene-7-octenal* **5c**. To a solution of (*S*)-3-(*N*-allyl-*N*-tosyl)amino-2-methylene-7-octen-1-ol (2.727 g, 7.81 mmol, 92% ee) in CH_2Cl_2 (80 mL) was added K-birnessite (23.4398 g). The reaction mixture was stirred at room temperature for 3 h. Black precipitate was removed by filtration over celite. The filtrate was concentrated in vacuo and then purified through flash chromatography (silica gel/hexane–EtOAc) to give **5c** in 90% yield (2.4419 g) as a pale yellow oil; enantiomeric purity was determined by HPLC analysis (230 nm, 40 °C) t_R 15.9 min (minor); t_R 29.1 min (major) [CHIRALPAK IC (0.46 cm × 25 cm) hexane–*i*PrOH, 80/20, 1.00 mL/min] as 90% ee. $[\alpha]_D$ −54.8 ($CHCl_3$, c 0.99); ^1H NMR ($CDCl_3$, 500 MHz) δ 9.37 (s, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 6.17 (s, 1H), 5.94–5.52 (m, 2H), 5.24–5.02 (m, 2H), 4.96 (d, J = 15.5 Hz, 1H), 4.94 (d, J = 8.7 Hz, 1H), 4.69 (t, J = 7.6 Hz, 1H), 3.86 (d, J = 6.3 Hz, 2H), 2.40 (s, 3H), 2.01 (q, J = 7.2 Hz, 2H), 1.96–1.68 (m, 2H), 1.44–1.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 193.4, 147.4, 143.1, 138.1, 138.0, 136.8, 135.4, 129.3, 127.5, 117.8, 114.9, 55.0, 48.6, 33.0, 31.0, 25.7, 21.4; IR (cm^{-1}); 2926, 1689, 1332, 1153, 910; HRMS (ESI MS M+1) m/z 348.1646. Calcd for $C_{19}H_{26}NO_3S$ 348.1633.