

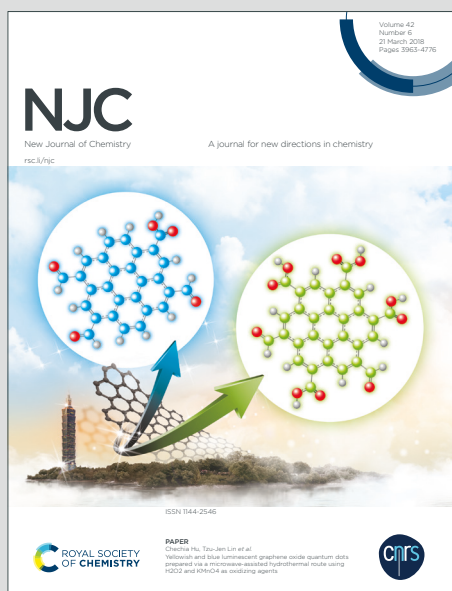
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COMMUNICATION

## KMnO<sub>4</sub>-catalyzed chemoselective deprotection of acetate and controllable deacetylation-oxidation in one-pot<sup>†</sup>

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Aakanksha Gurawa,<sup>a</sup> Manoj Kumar,<sup>a</sup> Dodla S. Rao,<sup>a</sup> and Sudhir Kashyap<sup>\*a</sup>

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A novel and efficient protocol for chemoselective deacetylation under ambient conditions has been developed by using catalytic KMnO<sub>4</sub>. The stoichiometric use of KMnO<sub>4</sub> highlights the dual-role of heterogeneous oxidant enabling the direct access to aromatic aldehydes in one-pot sequential deacetylation-oxidation. The reaction employing an alternative solvent system allows the clean transformation of benzyl acetate to sensitive aldehyde in a single step besides preventing the over-oxidation to acids. Use of inexpensive and readily accessible KMnO<sub>4</sub> as environmentally benign reagent and ease of reaction operation is particularly attractive, performing the controlled oxidation and facile cleavage of acetate in preceding step.

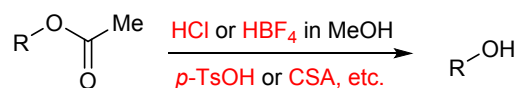
Selective manipulation and functional group inter-conversion have unique importance in modern organic synthesis especially in assembling complex molecular structures.<sup>1</sup> The hydroxyl group is ubiquitous and versatile structural unit, abundant in natural products predominantly in more complex molecules like carbohydrate based scaffolds.<sup>2</sup> Introducing an acetyl group on a free hydroxyl functionality remains the choice of transformation and routinely practice in synthetic chemistry laboratory preferably due to the ease of protection/deprotection.<sup>1,2</sup> However, the orthogonal acetylation as well selective removal in the presence of other esters such as benzoate, pivalate etc. is quite elusive and particularly important to accomplish a target synthesis.<sup>1-3</sup>

Over the decades, several protocols employing homogeneous reagents have been evolved for such transformations including diverse reaction conditions, (i) HCl/MeOH<sup>4</sup> (ii) DBU in benzene<sup>5</sup> (iii) guanidine in ethanol/dichloromethane<sup>6</sup> (iv) HBF<sub>4</sub>·Et<sub>2</sub>O in MeOH<sup>7</sup> (v) excess of Sm metal in combination of molecular iodine<sup>8</sup> (vi) 50% NH<sub>3</sub> in MeOH<sup>9</sup> (vii) NH<sub>2</sub>NH<sub>2</sub> in AcOH/pyridine<sup>10</sup> (viii) Bu<sub>3</sub>SnO under heating<sup>11</sup> (ix) Mg or Mg(OMe)<sub>2</sub> in MeOH<sup>12</sup> (x) *p*-TsOH or CSA

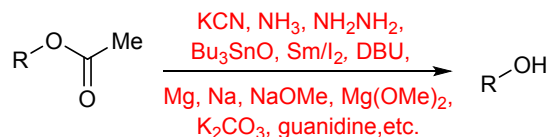
(1.0 equiv./acetate),<sup>13</sup> are quite a few to be cited (Scheme 1a, b). Despite the specific usefulness of these methods, employing excessive toxic/hazardous reagents and unconventional reaction operation, poor yields and selectivity, lack of substrate compatibility and tedious work-up process, have been unsolved issues. Besides, some of protocols predominantly rely on conventional yet strong acidic (Brønsted acids like HCl) or basic conditions including Zemplén hydrolysis (NaOMe in MeOH).<sup>1</sup> Although, selective removal of acetate is reported with Enzymes in specific conditions albeit with a restricted scope.<sup>14</sup> In this context, a catalytic and highly selective protocol employing inexpensive and environmentally friendly reagent system to confront current challenges and achieving green technology is highly desirable.

In continuation of our focus research in developing efficient and selective protocol emphasizing greener reagent system,<sup>15</sup> herein we present the first example of an oxidant KMnO<sub>4</sub>-catalyzed chemoselective acetyl deprotection under ambient reaction conditions (Scheme 1c).

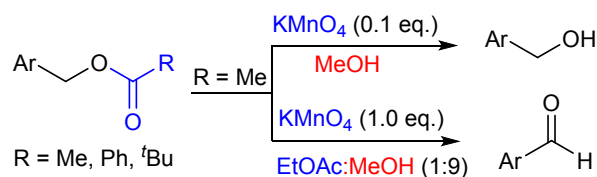
### a) Stoichiometric or excess acids



### b) Use of base/oxidant/hazardous-toxic reagents



### c) This work: KMnO<sub>4</sub> promoted deacetylation & oxidation



**Scheme 1.** Previous approaches for deprotection of acetate and chemoselective deacetylation using KMnO<sub>4</sub>.

<sup>a</sup> Carbohydrate Chemistry Research Laboratory (CCRL), Department of Chemistry, Malaviya National Institute of Technology, Jaipur-302017, INDIA. E-mail: skashyap.chy@mniit.ac.in, skr.kashyap@gmail.com.

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The protocol is facile and efficient representing an operationally simple one-pot deacetylation-oxidation of a wide range of benzyl-esters to their corresponding aldehydes under open air and reagent-controlled conditions. Notably, the present method is extremely attractive from a synthetic point of view as it allows the direct use of benzyl ester, a masked alcohol moiety, for diverse and rapid chemical transformations by employing a choice of reagent system.

To begin our investigation, we initially examined the deacetylation using 4-nitro-benzyl acetate **1a** (1.0 equiv.) as the model substrate in the presence of catalytic amount of MnO<sub>2</sub> (10 mol%). As summarized in Table 1, the experiment employing ethanol as the solvent resulted in a poor conversion after 24 h under open air conditions (entry 1). Subsequently, by switching the solvent to MeOH led to a slight improvement in the transformation, up to 30% (entry 2). The preliminary observations promoted us to standardization of the reaction conditions by varying the solvent system and catalyst/oxidant. Thus, the treatment of **1a** with 10 mol% of KMnO<sub>4</sub> in the presence of EtOH led to a significant improvement providing deacetylated product **2** with 70% conversion after 4 h (entry 3). A remarkable improvement was observed when the reaction was performed in methanol, facilitating the smooth and quantitative transformation providing the desired deprotected alcohol **2** albeit at ambient temperature after 1 h (entry 4).

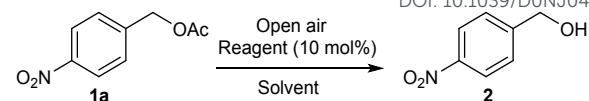
Further screening of solvent systems employing toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF, DMF, 1,4-dioxane or water found to be unsuccessful (entry 5-10). In contrast, reaction using CH<sub>3</sub>CN as the solvent was found to be too-sluggish and failed to effect desired conversion (entry 11). We next explored the applicability of a variety of complementary reagents and commonly used oxidants such as NaBO<sub>3</sub>, NaIO<sub>4</sub>, oxone, ammonium persulfate, *m*-CPBA, PhI(OAc)<sub>2</sub>, aq. H<sub>2</sub>O<sub>2</sub>, aq. TBHP, PCC, PDC, CAN, and DDQ (entry 12-23). In cases of NaBO<sub>3</sub>, TBHP, CAN and DDQ, a small 10-30% conversion was observed after 24 h, whereas, other reagents failed to give any significant transformation. Meanwhile, switching the open air system to nitrogen or argon atmosphere considerably diminished the reactivity of KMnO<sub>4</sub> affording a lower conversion (entry 24).

To further probe the possibility of chemoselective deprotection of acetate group, we evaluated a series of esters comprising benzoyl (**1b**), pivoyl (**1c**) and *tert*-butyrate (**1d**) derived from representative 4-nitro benzyl alcohol (Table 2). Interestingly, the ester groups in **1b-1d** found to be compatible, which unambiguously verified the chemoselectivity of acetate group under KMnO<sub>4</sub>-catalyzed optimum procedure. Indeed, other commonly used protecting groups such as benzyl ether (**1e**), mesyl (**1f**), *tert*-butyldimethylsilyl (TBS) (**1g**), 2-tetrahydropyranyl (**1h**) and trityl (**1i**) were fully stable under established reaction conditions. Moreover, the tolerance of these functionalities at higher amount of KMnO<sub>4</sub> (up to 1.0 equiv.) further highlights the synthetic advantage of chemoselective deacetylation protocol.

Table 1. Screening and evaluation of reaction condition.<sup>[a]</sup>

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Entry	Reagent	Solvent	Time	Conv. (%) <sup>[b]</sup>
1	MnO <sub>2</sub>	EtOH	24 h	10%
2	MnO <sub>2</sub>	MeOH	24 h	30%
3	KMnO <sub>4</sub>	EtOH	4 h	70%
4	<b>KMnO<sub>4</sub></b>	<b>MeOH</b>	<b>1 h</b>	<b>100%</b>
5	KMnO <sub>4</sub>	Toluene	24 h	NR
6	KMnO <sub>4</sub>	DCM	24 h	NR
7	KMnO <sub>4</sub>	THF	24 h	NR
8	KMnO <sub>4</sub>	DMF	24 h	NR
9	KMnO <sub>4</sub>	1,4-Dioxane	24 h	NR
10	KMnO <sub>4</sub>	H <sub>2</sub> O	24 h	NR
11 <sup>[c]</sup>	KMnO <sub>4</sub>	CH <sub>3</sub> CN	1 h	ND
12	NaBO <sub>3</sub> ·H <sub>2</sub> O	MeOH	24 h	30%
13	NaBO <sub>3</sub> ·5H <sub>2</sub> O	MeOH	24 h	30%
14	NaIO <sub>4</sub>	MeOH	24 h	Traces
15	Oxone	MeOH	24 h	Traces
16	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	MeOH	24 h	Traces
17	<i>m</i> -CPBA	MeOH	24 h	Traces
18	PhI(OAc) <sub>2</sub>	MeOH	24 h	NR
19	H <sub>2</sub> O <sub>2</sub> (35%)	MeOH	24 h	Traces
20	TBHP (70%)	MeOH	24 h	>20%
21	PCC or PDC	MeOH	24 h	NR
22	CAN	MeOH	24 h	30%
23	DDQ	MeOH	24 h	>5%
24 <sup>[d]</sup>	KMnO <sub>4</sub>	MeOH	12 h	>15%

<sup>[a]</sup>Reaction conditions: **1a** (50 mg, 0.25 mmol, 1.0 equiv.), solvent (1 mL), 25 °C under atmospheric pressure of air. Oxone: (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>); *m*-CPBA: *meta*-Chloroperbenzoic acid; TBHP: *tert*-Butyl hydroperoxide; PCC: Pyridinium chlorochromate; PDC: Pyridinium dichromate; CAN: Ceric ammonium nitrate; DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone; NR = No reaction. <sup>[b]</sup>The conversion based on the starting material **1a**. <sup>[c]</sup>ND = Not detected, decomposition of starting material. <sup>[d]</sup>The reaction was performed under nitrogen or argon atmosphere.

In order to establish the synthetic utility of novel method, a comparison of earlier reports and current protocol is presented (Table 2). Meanwhile, the use of 1 mol% KMnO<sub>4</sub> was sufficed for the removal of acetate group in 12 h (entry 2). Although, selective cleavage of allylic or primary-acetates can be achieved by employing excess of DBU in benzene solvent<sup>5</sup> at 60 °C after 45 h (entry 3).

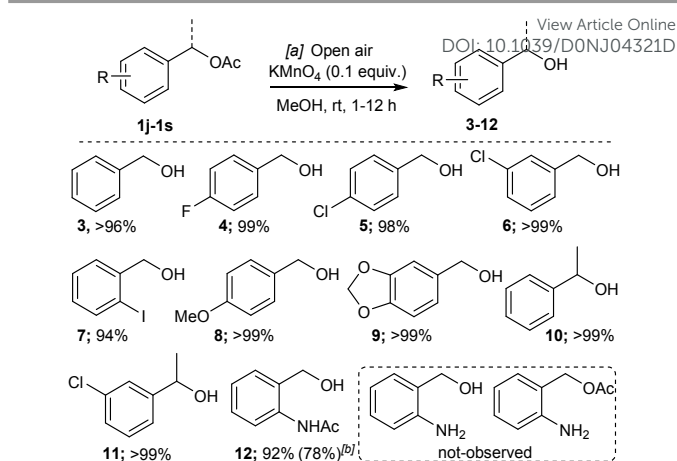
**Table 2.** Chemoselective deprotection of acetyl group.<sup>[a]</sup>

Entry	Reaction conditions	Substrate		
		1a	1b	1c
1	KMnO <sub>4</sub> (0.1 equiv.)/MeOH	✓	✗	✗
2	KMnO <sub>4</sub> (0.01 equiv.)/MeOH	✓	✗	✗
3	DBU/MeOH	✓	✗	✗
4	K <sub>2</sub> CO <sub>3</sub> /MeOH	✓	✓	✓
5	KCN/EtOH	✓	✓	✓
6	Mg/MeOH	✓	✓	✓
7	Sm, I <sub>2</sub> /MeOH	✓	✓	✓
8	Bu <sub>3</sub> SnOMe/DCE	✓	✓	✓
9	BF <sub>3</sub> ·Et <sub>2</sub> O/wet CH <sub>3</sub> CN	✓	✓	✓
10	MoO <sub>2</sub> Cl <sub>2</sub> /MeOH	✓	✓	✓

<sup>[a]</sup>Reaction conditions: **1a-1i** (50 mg, 1.0 equiv.), KMnO<sub>4</sub> (0.01-1.0 equiv.), MeOH (1 mL), 25 °C under atmospheric pressure of air, 1-12 h. NR = No reaction.

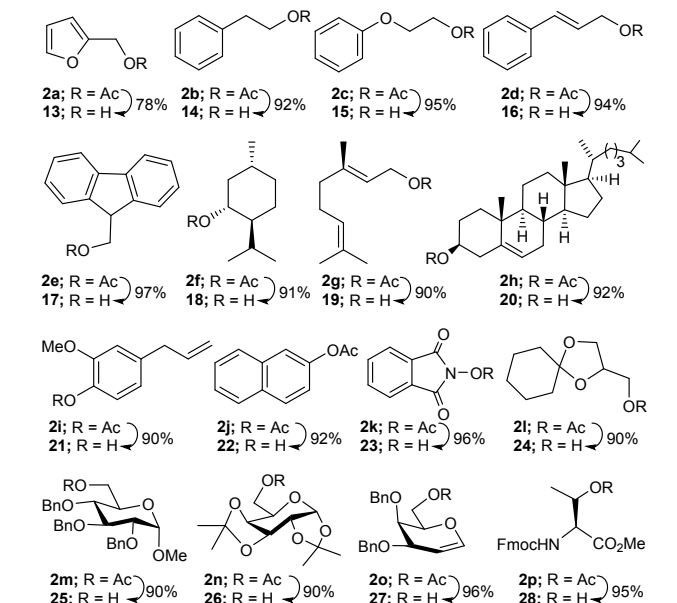
In contrast, other reagents such as K<sub>2</sub>CO<sub>3</sub> in methanol/water,<sup>16</sup> KCN in ethanol,<sup>17</sup> and Mg-metal or Mg(OMe)<sub>2</sub><sup>12</sup> could promote the deacetylation with moderate selectivity (entry 4-6). Likewise, excess of Sm-metal and I<sub>2</sub> are required to facilitate the deprotection of esters,<sup>8</sup> whilst, Bu<sub>3</sub>SnOMe in dichloroethane<sup>18</sup> or BF<sub>3</sub>·Et<sub>2</sub>O in wet acetonitrile<sup>19</sup> are effective for cleavage of anomeric acetates preferably over alkyl acetates (entry 7-9). Indeed, oxometallic reagents such as MoO<sub>2</sub>Cl<sub>2</sub> have been documented for trans-esterification<sup>20</sup> with discriminate selectivity (entry 10).

Having identified the chemoselective deacetylation, the generality and functional group compatibility of optimized procedure were examined using diverse functionalized aromatic acetates (Scheme 2). The substrates including benzyl acetates and diversely substituted halogen (F, Cl, I) underwent deacetylation smoothly affording the corresponding alcohols **3-7** in excellent yields. Aryl substrates with electron-rich moiety such as 4-methoxy and piperonyl acetate were reacted well to furnish the desired products **8** and **9** respectively in quantitative yields. Secondary acetates found to be highly amenable to the optimum conditions and cleaved in quantitative yields (products **10,11**). Of the note, chemoselective removal of *O*-Ac could be achieved successfully for a substrate bearing *N*-Ac without cleavage of amide ester (product **12**).



**Scheme 2.** Scope of chemoselective deacetylation; <sup>[a]</sup>Reaction conditions: **1j-1s** (1.0 equiv.), KMnO<sub>4</sub> (0.1 equiv.), MeOH (1 mL), 25 °C under atmospheric pressure of air, 1-12 h, the isolated and unoptimized yields. <sup>[b]</sup>The isolated yields after column chromatography.

To further demonstrate the potential synthetic applicability and generality, we next extended the scope for chemoselective deacetylation protocol. As illustrated in Scheme 3, virtually all the substrates investigated were reacted smoothly affording the desired products **13-28** in good yields (78-97%). The deacetylation of potentially sensitive heterocyclic compound such as furfuryl acetate (**2a**) performed well to access the corresponding furfuryl alcohol (**13**) in good yields. The deacetylation of potentially sensitive heterocyclic compound such as furfuryl acetate (**2a**) performed well to access the corresponding furfuryl alcohol (**13**) in good yields. The reaction employing substrates including alkylic (**2b,2c**) allylic (**2d**), 9-fluorenylmethyl (**2e**), and alicyclic such as menthyl acetate (**2f**) proceeded well to observe the clean deacetylation. Noteworthy, natural products comprising susceptible double bond such as geranyl (**2g**), cholesteryl (**2h**), and eugenyl acetate (**2i**) participated effectively, resulting the chemoselective cleavage of acetate.

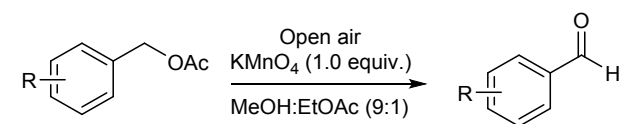


**Scheme 3.** Investigation of selective deacetylation and compatibility of diverse functionalities. Reaction conditions: **2a-2p** (1.0 equiv.), KMnO<sub>4</sub> (0.1 equiv.), MeOH (1 mL), 25 °C under atmospheric pressure of air, 1-12 h, the isolated and unoptimized yields.

Indeed, phenolic acetate (**2j**), N-acetoxy (**2k**), and a spiro substrate bearing dioxo functionality (**2l**), uniformly converted to their corresponding hydroxyl compounds under operationally facile protocol. Significantly, carbohydrate (**2m-2o**) and amino-acid (**2p**) molecules comprising relatively subtle or labile substituents (isopropylidene, enol-ether, Me-ester) were also deacetylated chemoselectively in good yields.

Next, we investigated the possibility of deacetylation-oxidation of benzyl acetates to obtain the aromatic aldehydes in one-pot process. Thus, treatment of **1a** with 10 mol%  $\text{KMnO}_4$  in MeOH for a longer reaction time (24 h) in open air provided a mixture of alcohol **2a** and oxidized aldehyde **29** with inconsistent ratios.<sup>21</sup> Further increasing the amount of  $\text{KMnO}_4$  (1.0 equiv.) led to a non-selective and over oxidation affording undesired complex reaction mixture of aldehydes and acids (**29a**). Subsequently, deacetylation and controlled oxidation of **1a** could be accomplished by performing the reaction in a mixed solvent system; MeOH:EtOAc (9:1) affording the corresponding aldehyde **29** in quantitative yields (Table 3, entry 1). It is pertinent to mention that, the selective and controlled-oxidation of alcohols have still retained as an important yet challenging transformation owing to the prominence and enhanced synthetic applicability in organic chemistry.<sup>22</sup>

Table 3.  $\text{KMnO}_4$ -promoted deacetylation-oxidation in one-pot.<sup>[a]</sup>



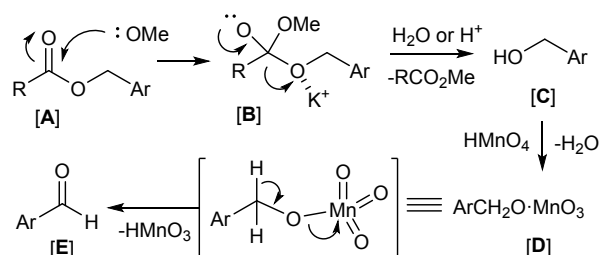
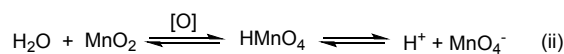
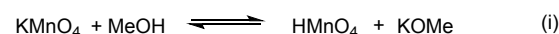
Entry	Substrate	Product; Yields <sup>[b]</sup>	Time
1	R = 4-NO <sub>2</sub>	<b>29</b> ; >99%	16 h
2	R = H	<b>30</b> ; >99%	18 h
3	R = 4-F	<b>31</b> ; >99%	20 h
4	R = 4-Cl	<b>32</b> ; >99%	24 h
5	R = 3-Cl	<b>33</b> ; 90%	12 h
6	R = 2-Cl	<b>34</b> ; 92%	20 h
7	R = 2-I	<b>35</b> ; 94% (98%) <sup>[c]</sup>	14 h
8	R = 2,4-Cl	<b>36</b> ; >99%	20 h
9	R = 4-OMe	<b>37</b> ; >99%	24 h
10	R = 3-OPh	<b>38</b> ; 94%	32 h
11	R = 2-NO <sub>2</sub>	<b>39</b> ; >99%	30 h
12	R = 3,5-NO <sub>2</sub>	<b>40</b> ; 90%	16 h
13	Piperonyl acetate	<b>41</b> ; 96% (92%) <sup>[c]</sup>	10 h
14	R = 2-NHAc	<b>42</b> ; >99% (84%) <sup>[d]</sup>	12 h

<sup>[a]</sup>Reaction conditions: **1** (50 mg, 1.0 equiv.),  $\text{KMnO}_4$  (1.0 equiv.), MeOH:EtOAc (9:1, 2 mL), 25 °C under atmospheric pressure of air for specify time. <sup>[b]</sup>The isolated and unoptimized yields. <sup>[c]</sup>The isolated yields for gram-scale reactions. <sup>[d]</sup>The isolated yields after column chromatography.

Following the results, we next demonstrated the extension of deacetylation-oxidation process for the conversion of benzyl acetates directly into their corresponding aldehydes in a single step. As summarized in Table 3, all the reactions employing substrates bearing electron-withdrawing and electron-donating functional groups (H, F, Cl, I, OMe, OPh, NO<sub>2</sub>), irrespective of the position on phenyl ring (mono- or di-substituted), were proceeded with almost quantitative yields (**30-40**) (entries 2-12). Likewise, piperonyl acetate was transformed into piperonal (**41**) in 96% yields, as a waxy solid (entry 13). Also worthy of mention that a substrate bearing diverse ester groups (OAc and NHAc) undergoes selective deacetylation and subsequent oxidation producing the corresponding aldehyde **42** in good yields (entry 13). The synthetic utility of deacetylation-oxidation method was further highlighted by conducting the gram-scale reactions of 2-iodobenzyl acetate and piperonyl acetate (entries 6, 13).

Although a detail mechanism for  $\text{KMnO}_4$ -mediated deacetylation-oxidation remains unclear and awaits further experimentations, a speculative rationalization based on literature analogy could be postulated. As presented in Scheme 4, the pertinent reducing characteristic of methanol towards  $\text{KMnO}_4$ ,<sup>23</sup> especially in neutral or slightly acidic conditions, would generate the permanganic acid ( $\text{HMnO}_4$ ) and potassium methoxide (KOMe) intermediate (eq. i). The higher oxidizing complex Mn(VII) dissociates into respective ions or disproportionate to Mn(II) and water, which then oxidized back to Mn(VII) with the atmospheric dioxygen molecule (eq. ii). Potassium methoxide generated from  $\text{KMnO}_4$  would proportionate with respective ionic species (eq. iii).

The subsequent nucleophilic attack of methoxide ion ( $\text{MeO}^-$ ) on electrophilic carbon of acyl substrate [**A**] and coordination of  $\text{K}^+$  with alkyl-oxygen ( $\text{ArCH}_2\text{-O}^-$ ) would unambiguously produce the tetrahedral intermediate [**B**]. The incipient transient species will breaks into respective aryl alkoxide ion ( $\text{ArCH}_2\text{O}^-$ ) by displacing the acyl group and simultaneously generating the deprotected alcohol [**C**], possibly by abstracting the proton from water molecule. Subsequently, the main oxidizing species ( $\text{HMnO}_4$ ) would then trap the alkanol [**C**] to give a penultimate intermediate complex ( $\text{ArCH}_2\text{O}\cdot\text{MnO}_3$ ) [**D**], which eventually



Scheme 4. A plausible rationalization for  $\text{KMnO}_4$ -promoted deacetylation-oxidation.



rearranged to aldehyde [E] and release  $\text{HMnO}_3$ . Further oxidation could be eliminated by diminishing the acidic conditions thus preventing the conversion of  $\text{Mn(V)}$  i.e.  $\text{HMnO}_3$  into higher-valent  $\text{Mn(VII)}$ ,<sup>23</sup> the later favors oxidation of aldehyde to acid.

In summary, we have established a mild and chemoselective deprotection of acetyl ester employing a catalytic amount of  $\text{KMnO}_4$  in open atmosphere at ambient temperature. The operationally convenient method tolerates electronically diverse functionalities and orthogonal with several sensitive protecting groups. The protocol is broadly applicable and successfully applied for a wide range of substrates enabling rapid and chemoselective deacetylation. The intrinsic dual-reactivity of  $\text{KMnO}_4$  leading to selective deacetylation and controlled-oxidation in one-pot process is amply useful. The improved protocol utilizing the environmentally benign chemicals is highly advantageous over conventional method ensuring the clean and quantitative transformation of benzyl acetates into corresponding aldehydes. We believe that these results will likely to contribute significantly in synthetic organic chemistry and find its utility as an alternative reagent system.

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## Experimental

### Representative procedure for the chemoselective deacetylation and one-pot deacetylation-oxidation;

A preformed solution of benzyl acetate **1** (50 mg, 1.0 equiv.) was treated with  $\text{KMnO}_4$  (0.1 equiv. for deacetylation in MeOH (1 mL) or 1.0 equiv. for deacetylation-oxidation in MeOH:EtOAc (9:1; 2 mL)). The mixture was stirred at room temperature in open air environment and the reaction progress was monitored by TLC. After the complete consumption of starting material was observed, typically 1-12 h for deacetylation and 10-32 h for deacetylation-oxidation, the reaction mixture was filtered and washed with EtOAc (10 mL). The resultant filtrate was treated with saturated aqueous  $\text{NaHCO}_3$  (5 mL), and aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with water and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo to obtain the analytical pure hydroxyl products **3-11** and **13-28** or aldehydes products **29-41**. For 2-acetamidobenzyl acetate, the crude residues were purified by silica gel column chromatography using EtOAc/Hexane to obtain the desired 2-acetamido benzyl alcohol (**12**) or 2-acetamidobenzaldehyde (**42**) following deacetylation-oxidation in one-pot.

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# *KMnO<sub>4</sub>-catalyzed chemoselective deprotection of acetate and controllable deacetylation-oxidation in one-pot*

*Aakanksha Gurawa, Manoj Kumar, Dodla Sivanageswra Rao,*

*and*

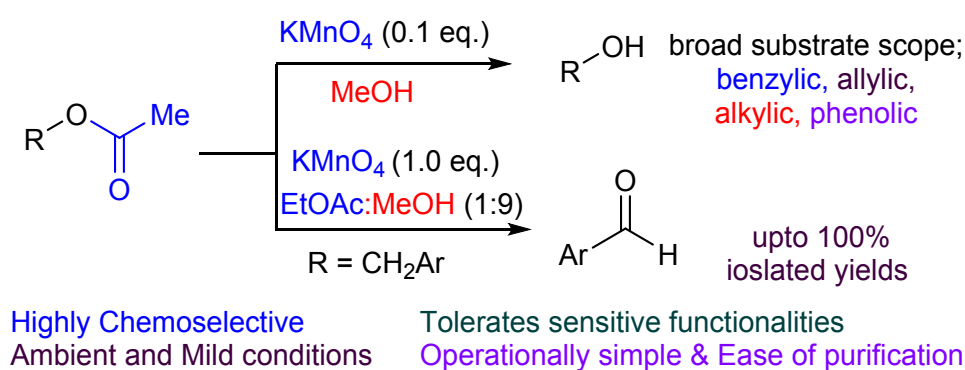
*Sudhir Kashyap\**

*Carbohydrate Chemistry Research Laboratory (CCRL), Department of Chemistry,*

*Malaviya National Institute of Technology (MNIT), Jaipur-302017, INDIA.*

*E-mail: [skashyap.chy@mnit.ac.in](mailto:skashyap.chy@mnit.ac.in), [skr.kashyap@gmail.com](mailto:skr.kashyap@gmail.com).*

## Graphical Abstract for Table of Contents



**Highly Chemoselective** and facile protocol for the deacetylation of a diverse range of substrates tolerating several sensitive functionalities have been accomplished under eco-friendly conditions.