



# Vanadium-catalyzed green oxidation of benzylic alcohols in water under air atmosphere



Kuniaki Marui<sup>a</sup>, Yuuki Higashiura<sup>a</sup>, Shintaro Kodama<sup>a</sup>, Suguru Hashidate<sup>a</sup>, Akihiro Nomoto<sup>a</sup>, Shigenobu Yano<sup>b</sup>, Michio Ueshima<sup>a</sup>, Akiya Ogawa<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

<sup>b</sup> Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

## ARTICLE INFO

### Article history:

Received 24 October 2013

Received in revised form 10 February 2014

Accepted 13 February 2014

Available online 20 February 2014

### Keywords:

Oxidation

Vanadium catalyst

Water solvent

Gram-scale

Air condition

## ABSTRACT

The oxidation of alcohols using catalytic amounts of metal complexes is highly attractive from the viewpoint of green chemistry principles. However, examples of metal complex-catalyzed oxidations of alcohols with O<sub>2</sub> using water as the solvent are still rare, and precious metals, high-pressure O<sub>2</sub> or air, and a stoichiometric amount of base are often required. In this study, it was found that an oxovanadium-4,4'-*t*-Bubpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) complex exhibited high catalytic activity in the oxidation of benzhydrols under an atmosphere of O<sub>2</sub> in water as the sole solvent. Interestingly, this catalytic oxidation method could be applied to the gram-scale aerobic oxidation of alcohols in water under the atmosphere.

© 2014 Elsevier Ltd. All rights reserved.

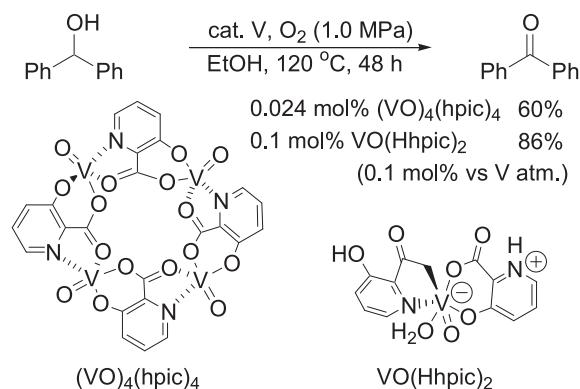
## 1. Introduction

The oxidation of alcohols to aldehydes and ketones is one of the most important synthetic transformations for organic chemists with respect to the useful intermediates obtained for the preparation of more complex organic compounds.<sup>1</sup> Conventionally, stoichiometric amounts of heavy metals (e.g., chromium(VI)) are used as oxidants. Therefore, the oxidation of alcohols using catalytic amounts of metal complexes is a highly attractive prospect from the viewpoint of green chemistry principles,<sup>2–7</sup> in which the following reaction characteristics are desired: (1) the use of earth-abundant transition metals in terms of sustainability and cost; (2) use of molecular oxygen (O<sub>2</sub>) as a terminal oxidant, where water is the only by-product; (3) use of water in place of organic solvents due to its low cost, inflammability, and great abundance.<sup>8</sup> However, examples of metal complex-catalyzed oxidations of alcohols with O<sub>2</sub> using water as the solvent are still rare.<sup>9</sup> Precious metals (e.g., Au, Ru, and Pd), high-pressure O<sub>2</sub> or air, and a stoichiometric amount of base are often required.

Vanadium is a relatively abundant element, ranking among the top 20 elements occurring in the earth's crust. The oxidative properties of pentavalent vanadium are well known.<sup>10</sup> Recent studies have focused on the development of vanadium catalysts for

the oxidation of alcohols with O<sub>2</sub>;<sup>11</sup> nonetheless, no reports are known to exist of an efficient vanadium catalytic system for aerobic oxidation of alcohols using water as the only solvent under atmospheric conditions.

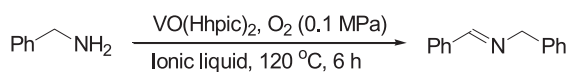
Recently, we have reported the aerobic oxidation of benzyl alcohols catalyzed by (VO)<sub>4</sub>(hpic)<sub>4</sub> or VO(Hhpic)<sub>2</sub>, which are synthesized from VOSO<sub>4</sub> and 3-hydroxypyridine-2-carboxylic acid (H<sub>2</sub>hpic).<sup>12a,b</sup> Recyclability was observed in (VO)<sub>4</sub>(hpic)<sub>4</sub>, while VO(Hhpic)<sub>2</sub> was noted to have relatively high catalytic activity (Scheme 1).



Scheme 1. Oxidation of benzhydrol using VO(Hhpic)<sub>2</sub> or (VO)<sub>4</sub>(hpic)<sub>4</sub>.

\* Corresponding author. Tel./fax: +81 72 254 9290; e-mail address: [ogawa@chem.osakafu-u.ac.jp](mailto:ogawa@chem.osakafu-u.ac.jp) (A. Ogawa).

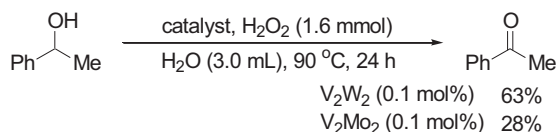
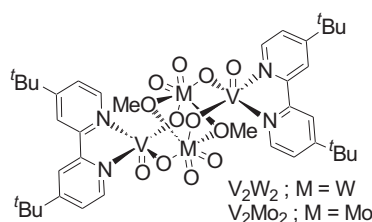
Opportunately, we also found that VO(Hhpic)<sub>2</sub> could also oxidize benzylamines to the corresponding imines with high selectivity using an ionic liquid solvent under an atmosphere of O<sub>2</sub> (0.1 MPa), also with good recyclability (Scheme 2).<sup>12c</sup>



**Scheme 2.** Oxidation of benzylamine using recyclable vanadium catalyst VO(Hhpic)<sub>2</sub> in ionic liquid.

Furthermore, the oxidation of alcohols with H<sub>2</sub>O<sub>2</sub> using heterotetranuclear complexes bearing bipyridyl ligands in water as solvent was already reported (Scheme 3).<sup>12d</sup>

Herein, we report the efficient oxidation of benzyl alcohol derivatives using an oxovanadium-2,2'-bipyridyl complex using water



**Scheme 3.** Oxidation of benzhydryl using heterotetranuclear complexes.

as the sole solvent under an atmosphere of O<sub>2</sub>; the ligand 4,4'-di-*tert*-butyl-2,2'-bipyridyl (4,4'-*t*-Bubpy) provides the greatest yields of oxidation products.<sup>12e</sup> Furthermore, this reaction system could also be used for gram-scale oxidation reactions under atmospheric pressure in air. To the best of our knowledge, this is the first report of an efficient catalytic system employing vanadium for the aerobic oxidation of alcohols using water as the only solvent under atmospheric conditions. We have also focused on using H<sub>2</sub>O as safer and abundant.

## 2. Results and discussion

Firstly, to determine the most effective ligand for catalysis, as preliminary experimental, a series of H<sub>2</sub>hpic analogues were screened (Table 1, entries 1–5). It was found that the pyridine unit was essential for the useful catalytic activity of vanadium (entry 5). An examination of several pyridine derivatives revealed that the functional group identity on the pyridine unit affects reaction efficiency to some extent (entries 6–9). Next, the bidentate 2,2'-bipyridyl ligand consisting of two pyridine units was applied to this oxidation. In entry 11, the yield of the corresponding ketone was found to have increased compared with entry 5. More interestingly, an over-oxidation product (benzoic acid) was observed when 2,2'-bipyridyl was used (entry 10). These data suggest that a bidentate ligand is more efficient than monodentate ligand in the oxidation, and that the bipyridyl unit in particular appears to be the most effective for the oxidative activity of vanadium.

A number of oxovanadium compounds including VO(Hhpic)<sub>2</sub>, previously identified as an oxidant with good catalytic activity (cf. Scheme 1), were examined in the oxidation of benzhydryl (1a) in water under an O<sub>2</sub> atmosphere (0.1 MPa) at 90 °C, and the resulting

**Table 1**

Examination of ligand effects on vanadium-catalyzed oxidation

|                        |        | VOSO <sub>4</sub> (2 mol%), ligand (4 mol%)<br>O <sub>2</sub> (1.0 MPa)<br>MeCN, 120 °C, 3 h |       |            |                        |
|------------------------|--------|--|-------|------------|------------------------|
| Ph-CH <sub>2</sub> -OH |        |  |       | Ph-C(=O)-H |                        |
| Entry                  | Ligand | Yield <sup>a</sup> (%)   | Entry | Ligand     | Yield <sup>a</sup> (%) |
| 1                      |        | 48   | 7     |            | 38                     |
| 2                      |        | 12   | 8     |            | 49                     |
| 3                      |        | 7  | 9     |            | 7                      |
| 4                      |        | 5  | 10    |            | 17 (29)                |
| 5                      |        | 40 (9)   | 11    |            | 55                     |
| 6                      |        | 55   |       |            |                        |

<sup>a</sup> Determined by <sup>1</sup>H NMR. Yield of benzoic acid is shown in parentheses.

products were identified by NMR. Unfortunately, VO(Hhpic)<sub>2</sub> and VOSO<sub>4</sub> were not effective under the reaction conditions (Table 2, entries 2 and 3). Also, the addition of H<sub>2</sub>hpic was found to be ineffective for the VOSO<sub>4</sub>-catalyzed reaction (entry 4). In sharp contrast, when 4,4'-*t*-Bubpy was used as a ligand, the oxidation of 1a proceeded successfully in moderate yield (entry 5). The addition of 4,4'-*t*-Bubpy was also effective for the VOSO<sub>4</sub>-catalyzed reaction (entry 6). A cursory examination of several bipyridyl derivatives in the oxidation reaction demonstrated that 4,4'-*t*-Bubpy was the

**Table 2**

Vanadium catalyst activities for oxidation of benzhydryl<sup>a</sup>

|              |   | catalyst (5 mol%), ligand (10 mol%)<br>O <sub>2</sub> (0.1 MPa)<br>H <sub>2</sub> O (0.5 mL), 90 °C |          |                              |  |
|--------------|---|---|----------|------------------------------|--|
| Ph-CH(OH)-Ph |   |   |          | Ph-C(=O)-Ph                  |  |
| 1a           |   |   |          | 2a                           |  |
| Entry        | Catalyst  | Ligand  | Time (h) | Yield of 2a <sup>b</sup> (%) |  |
| 1            | None  | None  | 3        | N.D.                         |  |
| 2            | VOSO <sub>4</sub>   | None  | 3        | Trace                        |  |
| 3            | VO(Hhpic) <sub>2</sub>  | None  | 3        | N.D.                         |  |
| 4            | VOSO <sub>4</sub>   | H <sub>2</sub> hpic   | 3        | Trace                        |  |
| 5            | [VO( <i>t</i> -Bubpy) <sub>2</sub> ] <sub>2</sub> SO <sub>4</sub> | None  | 3        | 43                           |  |
| 6            | VOSO <sub>4</sub>   | 4,4'- <i>t</i> -Bubpy   | 3        | 47                           |  |
| 7            | VOSO <sub>4</sub>   | 4,4'-DCbpy  | 3        | 2                            |  |
| 8            | VOSO <sub>4</sub>   | 6,6'-Mebpy  | 3        | N.D.                         |  |
| 9            | VOSO <sub>4</sub>   | 4,4'- <i>t</i> -Bubpy   | 6        | 83                           |  |
| 10           | VOSO <sub>4</sub>   | 5,5'-Mebpy  | 6        | 76                           |  |
| 11           | VOSO <sub>4</sub>   | 4,4'-Mebpy  | 6        | 33                           |  |
| 12           | VOSO <sub>4</sub>   | 4,4'-MeObpy   | 6        | 19                           |  |
| 13           | VOSO <sub>4</sub>   | 4,4'-Phbpy  | 6        | Trace                        |  |
| 14           | VOSO <sub>4</sub>   | Phen  | 6        | 22                           |  |
| 15           | VOSO <sub>4</sub>   | Bpy   | 6        | 17                           |  |

<sup>a</sup> Reaction conditions: catalyst (0.005 mmol), ligand (0.01 mmol), 1a (0.1 mmol), H<sub>2</sub>O (0.5 mL), O<sub>2</sub> (0.1 MPa), 90 °C.

<sup>b</sup> Determined by <sup>1</sup>H NMR. N.D.: not detected. 4,4'-DCbpy: 2,2'-bipyridyl-4,4'-dicarboxylic acid. 6,6'-Mebpy: 6,6'-dimethyl-2,2'-bipyridyl. 5,5'-Mebpy: 5,5'-dimethyl-2,2'-bipyridyl. 4,4'-Mebpy: 4,4'-dimethyl-2,2'-bipyridyl. 4,4'-MeObpy: 4,4'-dimethoxy-2,2'-bipyridyl. 4,4'-Phbpy: 4,4'-diphenyl-2,2'-bipyridyl. Phen: phenanthroline. Bpy: 2,2'-bipyridyl.

Download English Version:

<https://daneshyari.com/en/article/5216819>

Download Persian Version:

<https://daneshyari.com/article/5216819>

[Daneshyari.com](https://daneshyari.com)