Tetrahedron Letters 55 (2014) 5029–5032

Contents lists available at ScienceDirect

Tetrahedron Letters

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

# An efficient and reusable vanadium based catalytic system for room temperature oxidation of alcohols to aldehydes and ketones

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## ARTICLE INFO

*Article history:*
Received 20 April 2014
Revised 9 July 2014
Accepted 12 July 2014
Available online 18 July 2014

*Keywords:*
Vanadyl sulfate
Peroxovanadium complex
*tert*-Butyl hydroperoxide
Oxidation
Alcohols

## ABSTRACT

A simple and efficient vanadium based catalyst system for the oxidation of primary and secondary alcohols to aldehydes or ketones is reported using tert-butyl hydroperoxide as oxidizing agent and vanadyl sulfate as catalyst at room temperature. The versatility of the catalytic protocol is studied with wide variety of substrates.

In spite of its notable usefulness, homogeneous catalysis suffers from a number of drawbacks which lie in the removal and the reuse of the catalyst. Therefore development of catalytic system combining high catalytic efficiency with easy recovery and reuse of the catalytic species is a topic of great interest. Among the various organic transformations commonly encountered in contemporary organic synthesis, the controlled oxidation of alcohols to aldehydes and ketones, without forming over-oxidized product is one of the fundamental transformations with immense importance.[1] Conventionally, alcohol oxidation have been performed with stoichiometric amount of metal oxidants, notably permanganate,[2] bromate[3] or chromium[4] based reagents. These processes usually generate large amount of environmentally ill-disposed heavy-metal waste, and therefore they are not always favorable. Consequently various transition metals, for instance, Fe,[5] Mo,[6] Ru,[7] Pt,[8] Pd,[9] Ni,[10] Cu,[11] Au,[12] polyoxometalates,[13] Mn,[14] Rh,[15] Se,[16] Os[17] etc., catalyzed oxidation reactions using molecular oxygen,[18] $H_2O_2$[19] and *tert*-butyl hydroperoxide (TBHP)[20] as oxidizing agent are well explored. Various vanadium based catalytic systems such as, $VO(acac)_2$/MS 3 Å,[22a,b] V-Cu/DABCO,[22c] $VOCl_3$,[22d] $V_2O_5/K_2CO_3$,[22e] $VOSO_4$/TEMPO,[22f] $VOSO_4/NaNO_2$,[22g] $WO_3$-VPO,[22h] $VO(acac)_2$,[22i] Silica supported oxo-vanadium Schiff base,[22j] $V_2O_2$–$H_2O_2$,[22k] V-polyoxometalate[13b] etc., are effectively used for oxidation reactions. While considering cheaper and waste-free oxidant, $H_2O_2$ is found to be most suitable, as it produces water as the only byproduct. However, due to low stability and selectivity, most of the $H_2O_2$-mediated reactions rely on the use of inert condition and stoichiometric amount of oxidant. Conversely, TBHP was reported to be an effective oxidant for the selective oxidation of alcohols,[23–25] in presence of vanadium metal. Kaneda et al. showed that $VO(acac)_2$–TBHP system selectively catalyzed hydroxyl functional to carbonyl compounds.[23] Similarly, the selectivity of $V(O\text{-}i\text{Pr})_3$–TBHP was monitored by varying the amount of ligand, and cinnamaldehyde was achieved selectively (50% yield) with 45 mol % of *N*-hydroxy-*N*-methylbenzamide.[24] Later, vanadium supported on silica with TBHP was also reported as efficient catalytic system for alcohol oxidation.[25] Albeit of selectivity, use of hazardous solvents like benzene, $CCl_4$ etc.,[23] expensive ligand[24] and support[25] are some of the disadvantages of prime concern. In the contemporary chemistry, use of recoverable and reusable catalytic system is of main importance. Considering the above, herein, we report a new catalytic system for the oxidation of alcohols to aldehydes and ketones, employing $VOSO_4$ as catalyst and TBHP as oxidizing agent, at room temperature.

Initially, to investigate the effectiveness of the $VOSO_4$ in oxidation reaction, 1-phenylethanol (1 mmol) was chosen as a model substrate and the reaction was carried out using *tert*-butyl hydroperoxide (TBHP) as oxidant in presence of 10 mol % $VOSO_4$ at room temperature. The results are summarized in Table 1. The reaction was found to be very sluggish in water (Table 1, entry 1). However,

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http://dx.doi.org/10.1016/j.tetlet.2014.07.047
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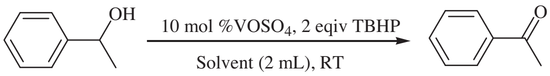
**Table 1**
Optimization of reaction condition for oxidation of 1-phenyl ethanol



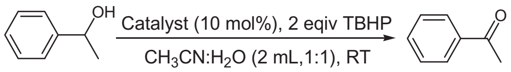
| Entry | Solvent | Time (h) | Yield[a] (%) |
|---|---|---|---|
| 1 | $H_2O$ | 24 | 47 |
| 2 | MeOH | 24 | 63 |
| 3 | $CH_2Cl_2$ | 24 | 60 |
| 4 | THF | 24 | 45 |
| 5 | DMF | 24 | 53 |
| 6 | DMSO | 20 | 81 |
| 7 | AcOH | 10 | 84 |
| 8 | $CH_3CN$ | 8 | 90 |
| 9[b] | $CH_3CN/H_2O$ | 5 | 96 |
| 10[c] | $CH_3CN/H_2O$ | 20 | 57 |
| 11[d] | $CH_3CN/H_2O$ | 20 | 70 |

[a] Isolated yield.
[b] 2 ml (1:1) solvent was used.
[c] 1 equiv TBHP was used.
[d] 5 mol % $VOSO_4$ was used.

we were able to isolate moderate yield of product in methanol (Table 1, entry 2). Similarly moderate yields were also obtained in dichloromethane, THF and DMF (Table 1, entries 3–5). However we were able to isolate 81% and 84% yield of the product in DMSO and acetic acid, respectively, (Table 1, entries 6 and 7). Interestingly, excellent conversion was observed in $CH_3CN$ (Table 1, entry 8) and we were able to isolate 90% yield of the product. To our delight, use of aqueous acetonitrile (1:1) yielded the expected acetophenone with 96% yield within very short reaction time (Table 1, entry 9). This observation may be attributed to solubility of $VOSO_4$ in water and organic alcohols in $CH_3CN$. However, decrease in yield to 57% was observed (Table 1, entry 10) when we reduced the amount TBHP to 1 equiv. Moreover 5 mol % of $VOSO_4$ is not sufficient for the complete conversion of 1-phenylethanol to acetophenone under the present reaction conditions (Table 1, entry 11).

We have also compared the efficiency of $VOSO_4$ with other vanadium sources and TBHP with hydrogen peroxide and the results are summarized in Table 2. Under these controlled reactions, 10 mol% of other vanadium sources viz. $V_2O_5$, $VO(acac)_2$ were used as catalyst in presence of 2 equiv of TBHP. It was observed that neither $V_2O_5$ nor $VO(acac)_2$ was as efficient as $VOSO_4$ to yield the product in shorter time (Table 2, entries 2 and 3). A similar reaction were carried out with $H_2O_2$ as oxidizing agent in presence of $VOSO_4$ catalyst, and only 35% of isolated product was observed (Table 2, entry 4). However, the reaction did not proceed in absence of $VOSO_4$ (Table 2, entry 5). The above experiments were found to be convincing enough to use $VOSO_4$ as better catalyst for oxidation of alcohols with TBHP.

**Table 2**
Oxidation of alcohol with different vanadium source



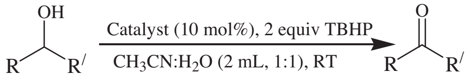
| Entry | Catalyst | Time (h) | Yield[a] (%) |
|---|---|---|---|
| 1 | $VOSO_4$ | 5 | 96 |
| 2 | $V_2O_5$ | 24 | 46 |
| 3 | $VO(acac)_2$ | 24 | 67 |
| 4[b] | $VOSO_4$ | 24 | 35 |
| 5 | – | 24 | Trace |

[a] Isolated yield.
[b] $H_2O_2$ was used as oxidizing agent.

Once the optimum reaction condition was achieved, various electronically diverse aromatic and aliphatic alcohols were subjected to oxidation with this present protocol[26] and the results are summarized in Table 3. Both secondary alcohols (Table 3, entries 1–6) and primary alcohols (Table 3, entries 7–11) gave the corresponding ketone and aldehydes, respectively, in excellent yield. No variation in yield was observed while changing the substituent. Most importantly, this protocol also worked well in case of aliphatic alcohol (Table 3, entries 12 and 13). Moreover aromatic alcohols can also be oxidized to the corresponding aldehydes with this catalytic system (Table 3, entry 14). Cyclic alcohol was converted to ketone efficiently (Table 3, entry 15). The newly developed catalytic system was effective for both 1,2-diols and 1,4-diols to give corresponding ketones in good yields (Table 3, entries 18–20). However, the protocol failed to selectively oxidize cinnamyl and propargyl alcohols, which resulted in a complex mixture of products (Table 3, entries 23 and 24). GCMS analysis indicated the epoxidation of alkene with cinnamyl alcohol. The new catalyst system was also effective for hex-5-en-1-ol (Table 3, entry 24).

In addition, the benzyl groups was found to be compatible under the present reaction condition and 2-(benzyloxy)ethane-1-ol was successfully oxidized to the corresponding aldehyde (Table 3, entry 21). This catalytic system is also applicable for the oxidation of cholesterol to the corresponding carbonyl compound in good yield (Table 3, entry 25). However this protocol failed to oxidize *N*-(2 hydroxyethyl)benzamide (Table 3, entry 22). Interestingly benzyl chloride also yielded corresponding aldehyde efficiently with this catalytic system (Table 3, entry 26). It is noteworthy to mention here that no over-oxidized product was observed in any of the alcohol studied.

**Table 3**
Oxidation of alcohols with the optimized reaction condition[a]



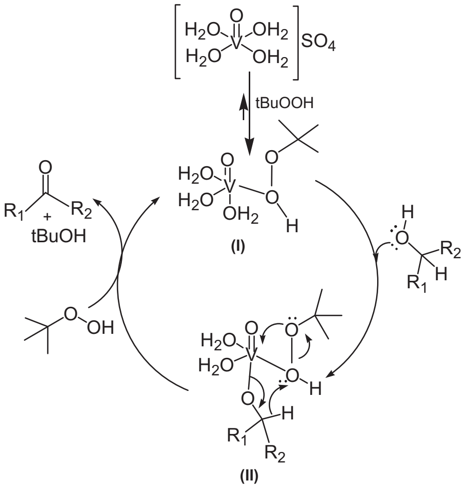
| Entry | R | R′ | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Ph | $CH_3$ | 5 | 96 |
| 2 | *p*-Cl-Ph | $CH_3$ | 8 | 90 |
| 3 | *p*-Br-Ph | $CH_3$ | 7 | 89 |
| 4 | *p*-$CH_3O$-Ph | $CH_3$ | 6 | 93 |
| 5 | Ph | PhCO | 5 | 91 |
| 6 | Ph | Ph | 6 | 95 |
| 7 | Ph | H | 3 | 88 |
| 8 | *p*-$NO_2$-Ph | H | 4 | 81 |
| 9 | *p*-Cl-Ph | H | 4 | 90 |
| 10 | *p*-$CH_3O$-Ph | H | 4 | 92 |
| 11 | *o*-OH-Ph | H | 5 | 82 |
| 12 | Octyl | H | 8 | 73 |
| 13 | Hexyl | H | 8 | 70 |
| 14 | Furyl | H | 7 | 80 |
| 15 | Cyclohexanol | | 6 | 94 |
| 16 | Propylene glycol | | 6 | 65 |
| 17 | Isoamyl alcohol | | 5 | 65 |
| 18 | Hexane-1,2-diol | | 8 | 85 |
| 19 | Hydrobenzoin | | 7 | 88 |
| 20 | Hexane-1,4-diol | | 6 | 70 |
| 21 | 2-(Benzyloxy)ethan-1-ol | | 5 | 79 |
| 22 | *N*-(2 Hydroxyethyl)benzamide | | 5 | – |
| 23 | Cinnamyl alcohol | | 6 | – |
| 24 | Propargyl alcohol | | 6 | – |
| 24 | Hex-5-en-1-ol | | 7 | 68 |
| 25 | Cholesterol | | 12 | 85 |
| 26 | Benzylchloride | | 7 | 82 |

[a] All the products were characterized by comparing the FTIR spectra, $^1H$ and $^{13}C$ NMR spectra, melting point measurement and high resolution GC–MS with authentic compounds.
[b] Isolated yield.

**Table 4**
Results of recycling experiments[27]

| Run[a] | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Time (h) | 5 | 5 | 5.5 | 5 | 5 | 5 |
| Yield[b] (%) | 96 | 95 | 96 | 96 | 94 | 94 |

[a] 1-Phenylethanol was used as substrate.
[b] Isolated yield.



**Scheme 1.** Plausible mechanism.

The reusability of catalyst is very important for cost reduction in process chemistry. We examined the reusability of the $VOSO_4$ and *tert*-butyl hydroperoxide system in oxidation reaction[27] and the results are incorporated in Table 4. In order to study the recyclability of the catalyst, after completion, the reaction mixture was extracted with ethyl acetate (10 mL) for three times to obtain the product in organic layer. Active catalytic species remained in aqueous layer, which was used for next run by adding required amount of fresh acetonitrile, substrate and TBHP. Remarkably, $VOSO_4$ could be reused successfully until the sixth run without either significant loss of yield or extension of the reaction time. This is a significant attribute of the present catalytic system.

Formation of peroxovanadium complex as an intermediate in oxidation reaction using peroxide is well established.[28,21c] In the present study, addition of tert-butyl hydroperoxide to the vanadyl sulfate gives a red-coloured solution which was assumed to be a peroxovanadate(V) complex and isolated by evaporating the solvent. The FTIR (see Supporting information) spectrum of the this complex shows sharp peaks at 986, 778 and 516 $cm^{-1}$ which indicate the presence of V=O, O—O(peroxide) and $V—O_2$, respectively.[29] The peaks at 3156 and 1615 $cm^{-1}$ are due to the presence of coordinated water. Again the UV–visible spectrum shows a LMCT band at 372 and 223 nm (see Supporting information). The observed spectra of the intermediate vanadium complex are in line with the oxomonoperoxo vanadate(V) reported earlier.[30] Based on these, a plausible mechanism involving oxomonoperoxo vanadate(V) complex is presented in Scheme 1. Reaction of butyl peroxide gives the oxobutylperoxovanadate(V) complex I which undergoes nucleophilic substitution of water (ligand) by alcohol (substrate) to form another intermediate II. Finally intermediate complex II gives the carbonyl compound.

In conclusion, we have developed a vanadyl sulfate promoted environmentally benign protocol for the controlled oxidation of primary and secondary alcohol to aldehydes and ketones, under mild reaction condition at room temperature. A wide range of alcohols with different substituents underwent oxidation efficiently. The catalytic system could be reused successfully until the sixth run without either significant loss of yield or extension of the reaction time. Use of aqueous solvent, no ligands and reusability of catalyst are some major advantages of the present protocol.

## Acknowledgments

We wish to thank UGC, New Delhi for support of this Project (No. 41 254/2012 (SR). G.S. thanks UGC for RFSMS fellowship. A.D. thanks Department of Science and Technology, New Delhi for support.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.07.047.

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26. *General procedure for oxidation of alcohol*: In a typical experiment, 1 mmol 1-phenyl ethanol and 10 mol % (25.30 mg) $VOSO_4 \cdot 5H_2O$ (purchased from Loba Chemie, molecular weight 253.08) in 2 ml $CH_3CN/H_2O$ (1:1) in a round bottomed flask. To this mixture 2 equiv 70% TBHP (aqueous) was added and stirred at room temperature for the time specified in Table 1. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 20 mL) three times. The ethyl acetate layer was dried with anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate–hexane as the eluent. Formation of the product was confirmed by comparing FTIR spectra, $^1H$ NMR spectra, $^{13}C$ NMR spectra, melting point measurement and GC–MS with authentic compounds.
27. *Experimental procedure for catalyst reusability study*: In a 100 mL round bottomed flask 3 mmol 1-phenylethanol was stirred with 10 mol % $VOSO_4$ in 6 mL $CH_3CN/H_2O$ (1:1). To this mixture, 2 equiv of TBHP was added. After the completion of the reaction the organic portion was extracted with ethyl acetate (3 × 10 mL). The remaining aqueous portion contains the catalyst and was reused for the next run with further addition of same amount of substrate, TBHP and acetonitrile. This process was repeated up to six cycles without loss of catalytic activity.
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