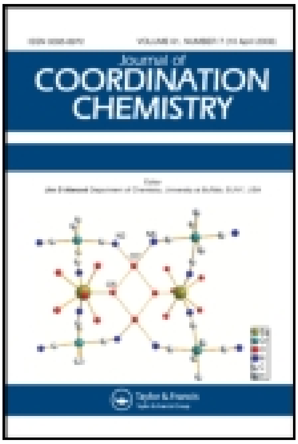

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A new vanadium Schiff base complex as catalyst for oxidation of alcohols

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A new vanadium Schiff base complex as catalyst for oxidation of alcohols

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The monoanionic bidentate Schiff base, *N*-(phenolyl)-benzaldimine (HL), has been employed to synthesize a new vanadium(IV) complex of general composition [VO(L)$_2$] (where L = O, N donor of Schiff base). The ligand and complex have been fully characterized by elemental analyses, molar conductance data, FT-IR, ^{1}H- and ^{13}C-NMR, and UV-Vis spectroscopies. Oxidation of alcohols to their corresponding aldehydes and ketones was conducted by this complex catalyst using Oxone as oxidant under biphasic reaction conditions (CH_2Cl_2/H_2O) and tetra-*n*-butylammonium bromide as phase transfer agent under air at room temperature.

Keywords: Bidentate Schiff base; Vanadium complex; Catalytic oxidation; Oxone

1. Introduction

Selective oxidation of alcohol to aldehydes and ketones is an important reaction in the laboratory and industry [1–4]. Traditionally, oxidizing reagents including dichromate and permanganate have been employed in order to accomplish this transformation [5, 6]. These reagents are moderately expensive, toxic, corrosive, unstable, without selectivity, dangerous to prepare, moisture-sensitive and tend to over-oxidize to carboxylic acids [7–9].

Transition metal complexes as catalysts in organic synthesis is an exciting field of research, and numerous reactions which are impossible to achieve by conventional synthetic methods have already been discovered [10–12]. There has been considerable interest in the chemistry of transition metal complexes of Schiff bases, due to the fact that Schiff bases stabilize many different metals in various oxidation states, controlling the performance of metals in useful transformations. Bidentate Schiff bases containing imine groups which can be used as modulators of structural and electronic properties of transition metal centers represent an important class of chelating ligands [13, 14].

Vanadium is an essential metal and exhibits great biological activity and potential medicinal applications when associated with certain metal–protein complexes, participating in oxygen transport, electron transfer reactions, or the storage of ions [15–19], creating enormous interest in study of systems containing this metal [20–28].

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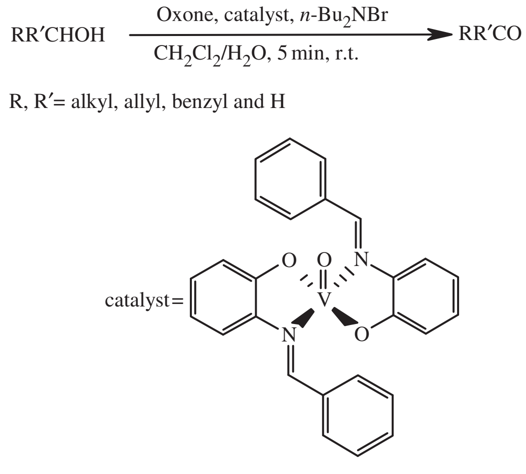


Scheme 1. The oxidation of alcohols by the $[VO(L)_2]$/Oxone/*n*-Bu_4NBr catalytic system.

However, activity of Schiff-base vanadium(IV) complexes toward catalytic oxidation in a homogeneous medium is not well documented with only a few vanadium(IV) Schiff-base complexes reported to be catalytically active toward alcohol oxidation [29].

In this article, we report the synthesis and characterization of the ligand, obtained from reaction of *benzaldehyde* with *o*-aminophenol, and its vanadium complex by physico-chemical methods and demonstrate the efficient and selective oxidation of alcohols to their corresponding aldehydes and ketones, using this bidentate Schiff-base vanadium complex under mild and biphasic conditions (CH_2Cl_2/H_2O) at room temperature with Oxone as oxidant (scheme 1).

2. Experimental

Chemical materials and solvents were purchased from Chemical companies, Fluka and Merck.

Elemental analyses (carbon, hydrogen, and nitrogen) were obtained from a Carlo ERBA Model EA 1108 analyzer. FT-IR spectra were obtained by using a Unicam Matson 1000 FT-IR spectrophotometer using KBr discs at room temperature. UV-Vis spectrum was recorded on a CARY 100 Bio VARIAN UV-Vis spectrophotometer in methanol. Molar conductances of the ligand and complex were determined in methanol (*ca* $10^{-3}\,\mathrm{mol\,L^{-1}}$) at room temperature using a Toa CM 405 conductivity meter. The ^{1}H- and ^{13}C-NMR spectra of the free ligand in $CDCl_3$ were obtained using a Bruker FT-NMR 500 MHz spectrometer. Melting points were taken on a Gallenkamp melting point apparatus. The reaction products of oxidation were determined and analyzed by a HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 lm × 0.25 lm) and flame-ionization detector.

2.1. *Synthesis of N-(phenolyl)-benzaldimine*

A solution of *o*-aminophenol (4.6 mmol, 0.50 g) in absolute EtOH (20 mL) was added to solution of benzaldehyde (4.6 mmol, 0.49 g) in absolute EtOH (20 mL) and the reaction mixture was refluxed at 80°C for 2 h. The solution was then evaporated to 15 mL and cooled to room temperature. The precipitated light yellow product was filtered off, washed with cooled ethanol and then dried in air. Yield: (87%); IR: 3329, 1623, 1580, 1481 cm^{-1}; ^1H-NMR ($CDCl_3$), δ: 8.75 (1H, s), 7.97 (2H, d), 7.54 (3H, m), 7.35 (1H, d), 7.27 (1H, t), 7.09 (1H, d), 6.97 (1H, t). ^{13}C-NMR ($CDCl_3$): 157.58, 152.80, 136.30, 135.95, 132.13, 129.39, 129.32, 129.27, 120.56, 116.33, and 115.47. Elemental Anal. Calcd for $C_{13}H_{11}NO$: C, 79.19%; H, 5.58%; N, 7.11%. Found: C, 79.09%; H, 5.54%; N, 7.02%. UV-Vis ($\lambda(\varepsilon$, $mol\,L^{-1}\,cm^{-1}$)): 216 (6559), 243 (10,543), 280 (5378), 341 (2612), Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 7.6, and m.p.: 87–89°C.

2.2. *Synthesis of [VO(L)$_2$]*

The ligand, HL (1.52 mmol) was dissolved in methanol (25 mL) and added to a methanol solution (20 mL) of [VO(acac)$_2$] (0.76 mmol) and the mixture was gently refluxed at 65°C for 3 h. After cooling, the resulting brown crystals were filtered and washed with cooled methanol and then dried in air. Yield: (63.17%). IR: 1595, 983 cm^{-1}, Elemental Anal. Calcd for $C_{26}H_{20}N_2O_3V$: C, 67.98%; H, 4.36%; N, 6.1%. Found: C, 67.81%; H, 4.39%; N, 6.02%. UV-Vis ($\lambda(\varepsilon$, $mol\,L^{-1}\,cm^{-1}$)): 215, 238, 265, 430, 590, and Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 1.4.

2.3. *Typical procedure*

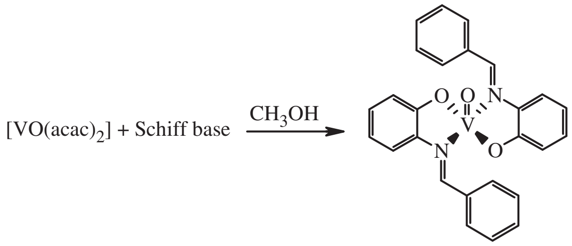
In a typical experiment, a solution of Oxone (0.2 mmol) in H_2O (5 mL) at room temperature was added to a solution of alcohol (0.2 mmol), tetra-*n*-butylammonium bromide (0.1 mmol), and [VO(L)$_2$] (0.01 mmol) in CH_2Cl_2 (1 mL), and the biphasic mixture stirred vigorously. Formation of products and consumption of substrates were monitored by GC. The identity of products was determined by comparison with authentic samples using gas–liquid chromatography. Oxidation product yields based on the oxidant were quantified by comparison with chlorobenzene.

3. Results and discussion

3.1. *Complex characterization*

A new vanadium(IV) complex, [VO(L)$_2$] (L = the anion of the Schiff base), has been prepared from [VO(acac)$_2$] (1 mol) and the Schiff base (2 mol) in methanol as shown in scheme 2. The complex is brown, stable to air and light and soluble in methanol, ethanol, acetonitrile, methylene chloride, DMF, and DMSO. The analytical data for the new complex (table 1) agrees very well with the proposed formula.

In order to study the binding mode of the Schiff base to vanadium in the new complex, IR spectra of the free ligand were compared with spectra of the vanadium complex. A strong band is observed in the free ligand at 1624 cm^{-1}, characteristic of



Scheme 2. Synthesis of complex [VO(L)$_2$].

Table 1. Microanalytical and spectral data for HL and [VO(L)$_2$].

	UV-Vis		C, H, N				Molar conductance
Ligand/complex	Solvent	λ (nm) ε (mol L^{-1} cm^{-1})	C (%)	H (%)	N (%)	IR (cm^{-1})	Λ_M (Ω^{-1} cm^2 mol^{-1})
$C_{13}H_{11}NO$ (HL)	C_2H_5OH	216 (6559)	79.09	5.54	7.02	υ(O–H) 3330	7.6
		243 (10,543)	(79.19)	(5.58)	(7.11)	υ(C=N) 1624	
FW = 240.26		280 (5378)					
m.p. = 87–89°C		341 (2612)					
[VO(L)$_2$]	C_2H_5OH	215, 238, 265	67.81	4.39	6.02	υ(O–H) Absent	1.4
$C_{26}H_{20}N_2O_3V$		430, 590	(67.98)	(4.36)	(6.1)	υ(C=N) 1595	
FW = 458.94						υ(V=O) 983	

azomethine (C=N) [30]. Coordination of the Schiff base to the metal through the azomethine nitrogen is expected to reduce the electron density in the azomethine and lower ν(C=N). In the spectra of the complex, ν(C=N) showed a negative shift to 1595 cm^{-1}, indicating coordination of the azomethine nitrogen to vanadium (table 1) [31, 32].

A medium intensity band, at 3330 cm^{-1} in the free ligand due to $\nu_{(OH)}$, was absent in the complex, indicating deprotonation of the Schiff base prior to coordination [31]. The complex exhibits characteristic and strong $\nu_{(V=O)}$ at 983 cm^{-1}, indicating that there is no intermolecular interaction with participation of the oxovanadium moiety [30].

Molar conductivities of ligand and its complex in methanol were 7.6 and 1.4 Ω^{-1} cm^2 mol^{-1}, respectively, and are given in table 1. These results show that the ligand coordinates to the metal ions to form a neutral coordination compound. Molar conductances are much smaller than those of 1 : 1 electrolytes [33], thus they are considered to be non-electrolytes.

Electronic spectra of the ligand and its complex were recorded in EtOH (table 1). The ligand exhibits intraligand transitions at ~280 nm due to $\pi \rightarrow \pi^*$ transitions and at ~341 nm due to $n \rightarrow \pi^*$ transitions [34]. On complexation, these bands due to the azomethine are shifted to lower energy, supporting coordination of the imine nitrogen [34, 35]. In the spectra of the complex, new bands at 430 nm can be attributed to charge transfer bands (ligand to metal or metal to ligand) [36]. Bands at 590 nm in the complex come from the d–d transition of vanadium(IV).

Table 2. The effect of the nature of solvent/H_2O on the oxidation of benzylalcohol by the $[VO(L)_2]$/Oxone/*n*-Bu_4NBr catalytic system.[a]

Entry	Solvent	Conversion (%)[b]
1	CH_2Cl_2	91
2	CH_3Cl	79
3	CH_3CN	85
4	C_6H_6	51
5	CH_3COCH_3	81
6	CCl_4	63
7	*n*-hexane	47

[a] The molar ratios for $[VO(L)_2]$: *n*-Bu_4NBr : benzylalcohol : Oxone are 1 : 10 : 20 : 20.
[b] Conversions (%) are measured after 5 min at room temperature.

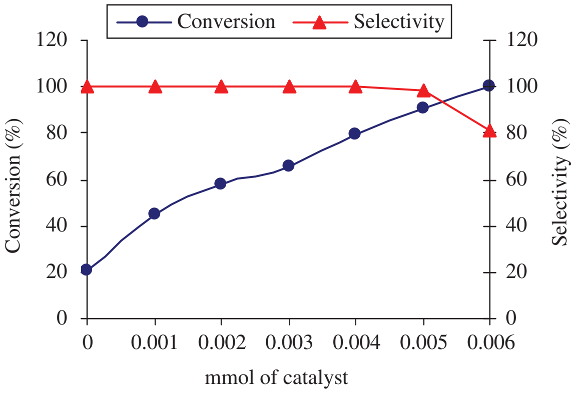


Figure 1. The effect of the amount of catalyst on oxidation of benzylalcohol by the $[VO(L)_2]$/Oxone/*n*-Bu_4NBr catalytic system. Reaction condition: benzylalcohol 0.2 mmol, Oxone 0.2 mmol, catalyst: *n*-$Bu_4NBr = 0.1$. Selectivity to benzaldehyde = (benzaldehyde%/(benzaldehyde% + benzoic acid%)) × 100.

3.2. *Catalytic reaction*

In order to evaluate catalytic activities of $[VO(L)_2]$ for oxidation of alcohols, the reactions were optimized for oxidation of benzylalcohol through investigation of the influence of solvent, the amount of catalyst, and the amount of Oxone.

3.2.1. Effect of solvent on the oxidation of benzylalcohol. For finding the best solvent under biphasic reaction conditions, dichloromethane, chloroform, acetonitrile, benzene, acetone, carbon tetrachloride, and *n*-hexane were employed as solvents. Among the solvents examined, dichloromethane was found to be the best for this protocol (table 2).

3.2.2. Optimization of amount of catalyst. Figure 1 illustrates the effect of amount of catalyst on the conversion and the selectivity of benzylalcohol oxidation, at room temperature for 5 min in CH_2Cl_2/H_2O. The conversion of benzylalcohol increases with the addition of catalyst from 0.001 to 0.005 mmol. When the amount of catalyst is increased to 0.006 mmol, the selectivity of benzylalcohol oxidation reduces from 98% to

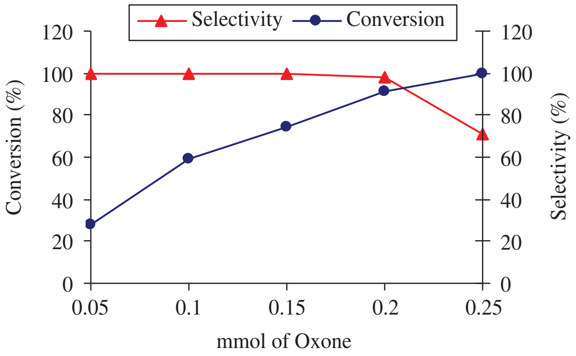


Figure 2. The effect of the amount of Oxone on oxidation of benzylalcohol by the $[VO(L)_2]$/Oxone/n-Bu_4NBr catalytic system. Reaction condition: benzylalcohol 0.2 mmol, catalyst 0.005 mmol, n-Bu_4NBr 0.05 mmol.

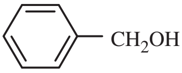
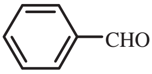
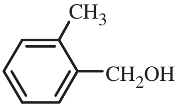
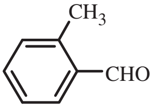
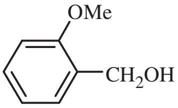
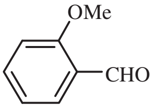
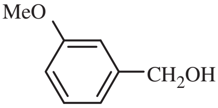
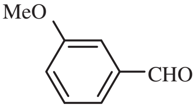
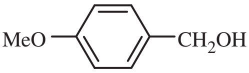
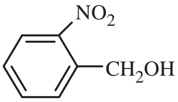
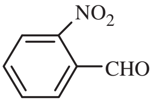
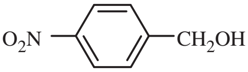
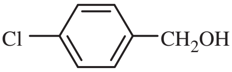
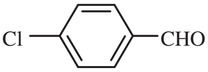
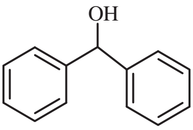
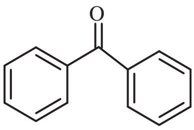
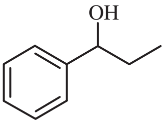
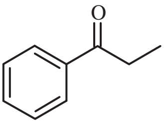
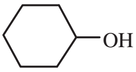
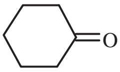
81%. The reaction without catalyst proceeds only very slightly. Hence, the amount of catalyst enhances the reaction rate for selective oxidation of benzylalcohol.

3.2.3. Optimization of amount of Oxone. The amount of Oxone could also affect the conversion and benzaldehyde selectivity (figure 2). When the amount of Oxone was increased from 0.05 to 0.2 mmol, the conversion of benzylalcohol increased from 28% to 91%. With a further increase of Oxone to 0.25 mmol, the selectivity to benzaldehyde decreases from 98% to 71%, although the conversion of benzylalcohol also increased from 91% to 100%.

3.2.4. Oxidation of alcohols with Oxone catalyzed by $[VO(L)_2]$. Reactions were performed at room temperature under air in CH_2Cl_2/H_2O containing $[VO(L)_2]$, tetra-n-butylammonium bromide, substrate, and Oxone in 1 : 10 : 20 : 20 molar ratio, respectively. The system was applicable for oxidation of a wide variety of primary and secondary alcohols to corresponding aldehydes and ketones (table 3).

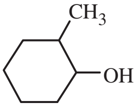
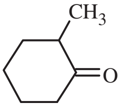
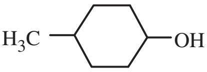
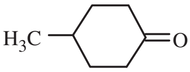
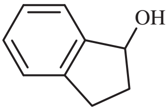
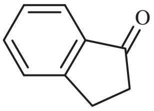
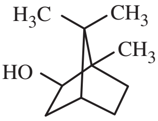
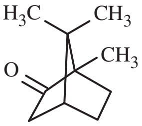
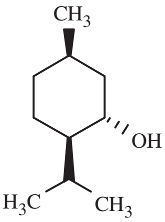
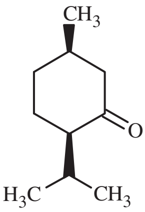
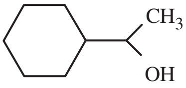
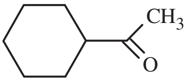
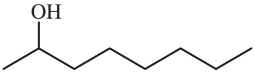
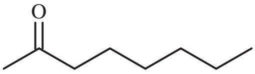
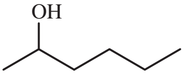
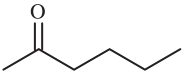
Benzylalcohols were oxidized to give the corresponding aldehydes with 86–98% conversion (entries 1–8). Substrates having electron-donating and -withdrawing substituents in the aromatic ring were compatible with this protocol. The change of nature and site of substituents (methyl, methoxy, chloro, and nitro) in the aromatic ring of benzylalcohol to probe the electronic effects displayed no regular trends in the conversion. The catalytic oxidation system can over-oxidize aldehyde product to carboxylic acid (2% for benzylalcohol oxidation at 5 min, table 3, entry 1). With the increase in the reaction time up to 30 min, more reduction of selectivity was observed due to over-oxidation (e.g., 9% benzoic acid is formed in the benzylalcohol oxidation after 30 min). Aliphatic alcohols and secondary alcohols were less reactive in comparison to aromatic alcohols (entries 9–19). Secondary alcohols, e.g., diphenylmethanol and 1-phenylpropanol, could be converted to the corresponding ketones in 76–80% conversion (entries 9 and 10). Oxidations of borneol and 2-isopropyl-5-methylcyclohexanol require longer reaction time (30 min) to afford the corresponding ketones (entries 15 and 16).

Table 3. Oxidation of alcohols by the $[VO(L)_2]$–Oxone–*n*-Bu_4NBr catalytic system.[a]

Entry	Substrate	Product	Conversion (%)[b] (TON)[c]	Selectivity to aldehyde (%)[d]
1			91(18.2)	98
2			95(19)	97
3			96(19.2)	96
4			91(18.2)	98
5			98(19.6)	97
6			86(17.2)	100
7			89(17.8)	100
8			92(18.4)	98
9			80(16)	100
10			76(15.2)	100
11			63(12.6)	100

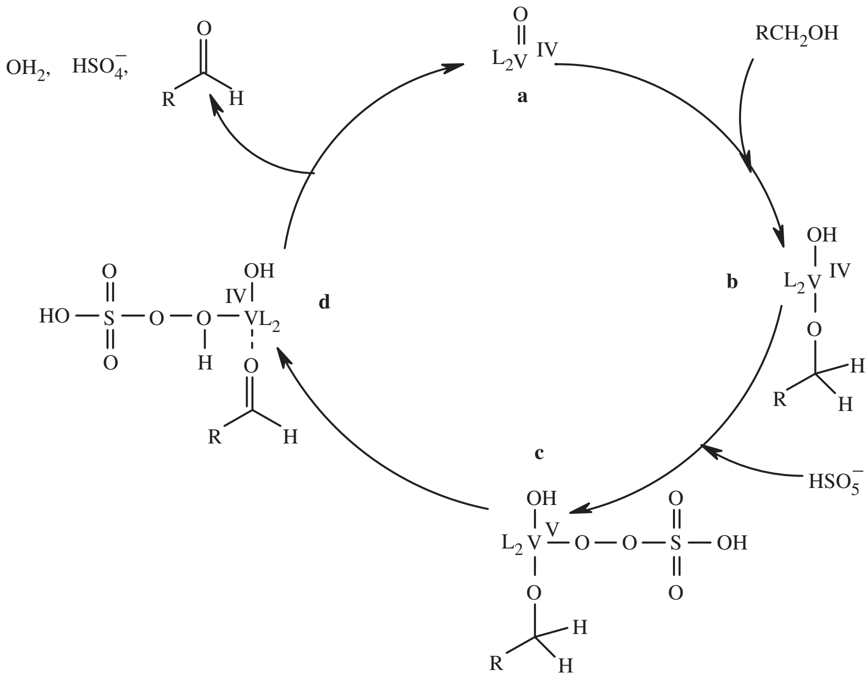
(*Continued*)

Table 3. Continued.

Entry	Substrate	Product	Conversion (%)[b] (TON)[c]	Selectivity to aldehyde (%)[d]
12			68(13.6)	100
13			72(14.4)	100
14			75(15)	100
15			61[e](12.2)	100
16			59[e](11.8)	100
17			71(14.2)	100
18			63(12.6)	100
19			61(12.2)	100

[a] The molar ratio for $[VO(L)_2]$: n-Bu_4NBr : benzylalcohol : Oxone is 1 : 10 : 20 : 20.
[b] Conversions (%) are measured relative to the starting alcohol after 5 min.
[c] mmol of product/mmol of catalyst.
[d] Selectivity to benzaldehyde = (aldehyde%/(aldehyde% + carboxylic acid%)) × 100.
[e] The reactions were run for 30 min at room temperature.

Exact mechanism for the catalytic oxidation of alcohols catalyzed by oxovanadium(IV) complex in the presence of Oxone is not clear at present. However, based on the nature of oxidation products, optimization results that indicate the reaction yield depends on both catalyst and oxidant concentration, and previously



Scheme 3. Proposed mechanism for alcohol oxidation by the $[VO(L)_2]$/Oxone/*n*-Bu_4NBr catalytic system.

reported mechanism [37, 38], a catalytic cycle is proposed in scheme 3. The alcohol can coordinate to $[VOL_2]$, **a**, to provide the complex **b**. Then **b** reacts with Oxone to give a corresponding intermediate **c** that can readily undergo intramolecular hydrogen abstraction to give the intermediate **d**. Finally, with separation of aldehyde or ketone, water and hydrogen sulfate of intermediate **d** and regeneration of catalyst **a**, the catalytic cycle is completed.

4. Conclusion

The complex $[VO(L)_2]$ has been synthesized and characterized by physico-chemical methods. We have demonstrated the effectiveness of a vanadium(IV) complex as catalyst for oxidation of different alcohols to carbonyl compounds with Oxone. Easy preparation, mild reaction condition, high yields of the products, short reaction time, no further oxidation to the corresponding carboxylic acids, high selectivity, and an inexpensive system make this catalytic system a useful method for oxidizing alcohols.

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