

# Efficient and selective oxidation of alcohols with *tert*-BuOOH catalyzed by a dioxomolybdenum(VI) Schiff base complex under organic solvent-free conditions

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**Abstract** The catalytic activity of dioxidobis{2-[(*E*)-*p*-tolyliminomethyl]phenolato}molybdenum(VI) complex was studied, for the first time, in the selective oxidation of various primary and secondary alcohols using tert-BuOOH as oxidant under organic solvent-free conditions at room temperature. The effect of different solvents was studied in the oxidation of benzyl alcohol in this catalytic system. It was found that, under organic solvent-free conditions, the catalyst oxidized various primary and secondary alcohols to their corresponding aldehyde or ketone derivatives with high yield. The effects of other parameters such as oxidant and amount of catalyst were also investigated. Among different oxidants such as H<sub>2</sub>O<sub>2</sub>, NaIO<sub>4</sub>, tert-BuOOH, and H<sub>2</sub>O<sub>2</sub>/urea, tert-BuOOH was selected as oxygen donor in the oxidation of benzyl alcohol. Also, it was found that oxidation of benzyl alcohol required 0.02 mmol catalyst for completion. Dioxomolybdenum(VI) Schiff base complex exhibited good catalytic activity in the oxidation of alcohols with tert-BuOOH under mild conditions. In this catalytic system, different primary alcohols gave the corresponding aldehydes in good yields without further oxidation to carboxylic acids.

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## Introduction

Aldehydes and ketones represent an important class of products and intermediates in the fine chemicals and specialties industry [1]. Therefore, selective oxidation of alcohols to their corresponding aldehydes and ketones is one of the most important fundamental reactions in organic chemistry at both laboratory and industrial level, and numerous methods have been developed using a variety of reagents for this purpose [2–8]. In traditional oxidation processes, large amounts of toxic and volatile organic solvents and inorganic oxidants (i.e.  $CrO_3$ ,  $KMnO_4$ , NaClO,  $MnO_2$ , etc.) were extensively used [9]. However, these oxidants are toxic, hazardous to handle, expensive, and lack selectivity, and large amounts of waste are generated [10]. From the environmental friendliness point of view, development of clean and green oxidants such as TBHP,  $H_2O_2$  or  $O_2$  has attracted increasing attention [11, 12]. In recent years, solvent-free organic reactions have attracted great interest because of their various advantages such as high efficiency and selectivity, easy separation and purification, mild reaction conditions, reduction in waste, simplicity in progress and handling, and benefits to the industry as well as the environment [13–15].

The ability of molybdenum to form stable complexes with Schiff base ligands led to the development of molybdenum Schiff base complexes which are efficient catalysts in both homogeneous and heterogeneous reactions [16–19]. In this area, dioxomolybdenum(VI) complexes have been particularly investigated because of their good catalytic activity for selective oxidation [20]. Recently, several dioxomolybdenum(VI) complexes have been used as catalysts in various oxidation reactions, such as epoxidation of olefins and oxidation of sulfides [21–25]. However, studies on oxidation of alcohols with dioxomolybdenum(VI) complexes as catalysts are still very limited [26].

In the present work, selective oxidation of alcohols to aldehydes and ketones with *tert*-BuOOH (TBHP) in the presence of a dioxomolybdenum(VI) Schiff base complex as catalyst under organic solvent-free conditions is reported (Scheme 1). In this catalytic system, the effect of different solvents, oxidants, and amount of catalyst was also studied.

## Experimental

### Materials and preparation of catalyst

All materials were of commercial reagent grade and obtained from Merck or Fluka. The Schiff base ligand 2-(*p*-tolyliminomethyl)phenol was prepared by the standard procedure of refluxing ethanolic solution of salicylaldehyde and *p*-tolylamine in 1:1 molar ratio. The dioxo-Mo(VI) Schiff base complex was prepared according to the published procedure by adding the Schiff base ligand and MoO<sub>2</sub>(acac)<sub>2</sub> (molar ratio 2:1) to dry methanol (25 ml), followed by refluxing for 1 h [27]. Light-yellow crystals of the complex were filtered off and recrystallized from absolute methanol



 $R_1 = alkyl$ , aryl, heteroaryl  $R_2 = H$ , alkyl

Scheme 1 Selective oxidation of alcohols by dioxo-Mo(VI) Schiff base complex

with yield of 76 % (0.57 g). Anal. calcd. for  $C_{28}H_{24}MoN_2O_4$  (%): C, 61.32; H, 4.41; N, 5.11. Found: C, 61.10; H, 4.15; N, 4.94.

#### **Physical measurements**

Fourier-transform infrared (FT-IR) spectrum (KBr pellets) was obtained with a Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer in the range of 400–4000 cm<sup>-1</sup>. The ultraviolet–visible (UV–Vis) spectrum of the complex was recorded in methanol solution using a T80 UV–Vis spectrophotometer. Elemental analysis was carried out on a Vario EL III CHNS elemental analyzer. Single-crystal X-ray data for the complex were collected at 296 K on a STOE IPDS II diffractometer with Mo K<sub> $\alpha$ </sub> ( $\lambda = 0.71073$  Å) radiation. The purity of the products and the progress of reaction were measured by thin-layer chromatography (TLC) using silica-gel Polygram SILG/UV254 plates. Gas chromatography (GC) experiments were performed with a Philips GC-PU 4600 instrument using 2 m column packed with silicon DC-200 with a flame ionization detector (FID).

#### General procedure for selective oxidation of alcohols

A typical experimental procedure was as follows: alcohol (1 mmol) as substrate was added to the dioxo-Mo(VI) Schiff base complex (0.02 mmol). Then, *tert*-BuOOH (1 mmol, 70 % aqueous solution) was added and the mixture was stirred at room temperature (25 °C). The progress of the reaction was monitored by thin-layer chromatography (TLC) (eluent *n*-hexane:ethyl acetate, various ratios). After the reaction was completed, the residue was washed with a minimal volume of  $CH_2Cl_2$ .

The solvent was then evaporated, and the pure product was obtained after chromatography on a silica gel column.

#### **Results and discussion**

#### **Characterization of catalyst**

In the FT-IR spectrum of the dioxo-Mo(VI) Schiff base complex (Fig. S1), the azomethene (C=N) band was observed at 1604 cm<sup>-1</sup> and the band at 1500 cm<sup>-1</sup> can be attributed to the aromatic rings in the Schiff base ligand. Also, the presence of two bands at 906 and 956 cm<sup>-1</sup> is due to Mo=O vibrations.

In the UV–Vis spectrum of the dioxo-Mo(VI) Schiff base complex (Fig. S2), peaks at 230 and 270 nm are assigned to benzene  $\pi \to \pi^*$  and imine  $\pi \to \pi^*$  transitions, respectively. The third peak at 340 nm is attributed to the O(p<sub> $\pi$ </sub>)  $\to$  Mo(d<sub> $\pi$ </sub>) charge-transfer transition [28, 29].

The crystal structure of the dioxo-Mo(VI) Schiff base complex was also confirmed by single-crystal X-ray diffraction (CCDC 792575) [27].

#### Catalytic oxidation of alcohols

To explore the catalytic activity of the dioxo-Mo(VI) Schiff base complex, benzyl alcohol was used as model substrate. First, different solvents were examined in the presence of dioxo-Mo(VI) Schiff base complex and *tert*-BuOOH (70 % aqueous solution) (Table 1). The results showed that use of a less-polar solvent such as toluene or chloroform afforded high yields of benzaldehyde (entries 1, 2), but lower yield of benzaldehyde was obtained using polar solvents such as methanol, acetone, and acetonitrile (entries 3–5). Interestingly, it was found that the highest yield of benzaldehyde was obtained under organic solvent-free conditions (entry 6).

Entry	Solvent	Dipole moment (D)	Time (h)	Alcohol conversion (%)	Benzaldehyde selectivity (%)	Benzaldehyde yield (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
1	Toluene	0.36	2	73	96	70	35	17.5
2	CHCl <sub>3</sub>	1.15	2	55	96	53	26.5	13.25
3	CH <sub>3</sub> OH	1.69	2	47	94	45	22.5	11.25
4	CH <sub>3</sub> COCH <sub>3</sub>	2.88	2	18	83	15	7.5	3.75
5	CH <sub>3</sub> CN	3.92	2	12	83	10	5	2.5
6	Solvent free	-	2	92	98	90	45	22.5

 Table 1
 Effect of solvent on oxidation of benzyl alcohol with tert-BuOOH catalyzed by dioxo-Mo(VI)

 Schiff base complex

Reaction conditions: benzyl alcohol (1 mmol), *tert*-BuOOH (1 mmol, 70 % aqueous solution), catalyst (0.02 mmol), solvent (1 ml), at room temperature (25 °C)

<sup>a</sup> Isolated yield

Entry	Catalyst amount (mmol)	Time (h)	Alcohol conversion (%)	Benzaldehyde selectivity (%)	Benzaldehyde yield (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
1	0	2	8	62	5	_	_
2	0.01	2	75	86	65	65	32.5
3	0.02	2	92	98	90	45	22.5
4	0.03	2	93	98	91	30.5	15.15

 Table 2
 Optimization of catalyst amount in oxidation of benzyl alcohol with *tert*-BuOOH catalyzed by dioxo-Mo(VI)
 Schiff base complex under organic solvent-free conditions

Reaction conditions: benzyl alcohol (1 mmol), *tert*-BuOOH (1 mmol, 70 % aqueous solution), catalyst, at room temperature (25 °C)

<sup>a</sup> Isolated yield

 Table 3
 Effect of various oxidants on oxidation of benzyl alcohol with *tert*-BuOOH catalyzed by dioxo-Mo(VI)

 Schiff base complex under organic solvent-free conditions

Entry	Oxidant	Time (h)	Alcohol conversion (%)	Benzaldehyde selectivity (%)	Benzaldehyde yield (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
1	NaIO <sub>4</sub>	2	35	86	30	15	7.5
2	$H_2O_2$	2	50	96	48	24	12
3	H <sub>2</sub> O <sub>2</sub> /urea (UHP)	2	78	96	75	37.5	18.75
4	<i>tert</i> -BuOOH (TBHP) (70 % aqueous solution)	2	92	98	90	45	22.5
5	No oxidant	2	12	83	10	5	2.5

Reaction conditions: benzyl alcohol (1 mmol), oxidant (1 mmol), catalyst (0.02 mmol), at room temperature (25  $^{\circ}\rm{C})$ 

<sup>a</sup> Isolated yield

The effect of reaction parameters was examined by performing the reaction in organic solvent-free conditions. We optimized the amount of catalyst in the oxidation of benzyl alcohol. The results showed that, when 0.02 mmol (11 mg) catalyst was used in the oxidation of benzyl alcohol, the highest yield of benzaldehyde was obtained, whereas trace amount of products (5 %) were detected when the same reaction was carried out in the absence of catalyst (Table 2).

The effect of different oxidants such as NaIO<sub>4</sub>,  $H_2O_2$ ,  $H_2O_2$ /urea (UHP), and *tert*-BuOOH (70 % aqueous solution) was also investigated in the oxidation of benzyl alcohol. The results showed that *tert*-BuOOH (TBHP) is the best oxygen source (Table 3).

Under the optimized reaction conditions, different primary and secondary alcohols were oxidized by this catalytic system. The results are summarized in Table 4.

It was found that various types of primary benzylic alcohols including those bearing electron-withdrawing and electron-donating groups were selectively converted to their corresponding aromatic aldehydes in good to high yields. In comparison with the electron-withdrawing groups at *para*-position for benzylic

Entry	Alcohol	Product <sup>b</sup>	Time	Alcohol	Selectivity (%)	Yield (%) <sup>c</sup>	TON	TOF
			(h)	conversion (%)				(h-1)
1	CH2OH	СНО	2	92	98	90	45	22.5
2	MeO CH <sub>1</sub> OH	MeO CHO	2	98	97	95	47.5	23.75
3	(Me) <sub>2</sub> C	(Me) <sub>2</sub> C	2	95	97	92	46	23
4	СП	CL	2	90	94	85	42.5	21.25
5	O2N CH1OH	O2N CHO	2	78	96	75	37.5	18.75
6	ОН	Сно	2	75	93	70	35	17.5
7	OH		3	78	100	78 <sup>d</sup>	39	13
8	OH	<u> </u>	3	82	100	82 <sup>d</sup>	41	13.67
9	OH	<u> </u>	3	75	100	75 <sup>d</sup>	37.5	12.5
10	OH		3	70	100	70 <sup>d</sup>	35	11.67

Table 4 Selective oxidation of alcohols with *tert*-BuOOH catalyzed by dioxo-Mo(VI) Schiff base complex under organic solvent-free conditions<sup>a</sup>

Reaction conditions: alcohol (1 mmol), tert-BuOOH (1 mmol, 70 % aqueous solution), catalyst (0.02 mmol), at room temperature (25  $^{\rm o}{\rm C}$ )

<sup>a</sup> All products identified by comparison of their physical and spectral data with those of authentic samples

<sup>b</sup> Isolated yield of corresponding aldehyde or ketone

<sup>c</sup> Determined by GC

alcohols, the electron-donating groups seemed to be more favorable for the formation of carbonyl compounds (entries 1–5, Table 4). Furthermore, furfuryl alcohol, a heteroaromatic alcohol which is considered to be a highly challenging substrate in most transition-metal catalyst systems, was oxidized to furfural in good yield in this catalytic system (entry 6, Table 4). As shown in Table 4, this system was found to be efficient for the oxidation of secondary alcohols. In this oxidation reaction the corresponding ketones were obtained in relatively good yields



Scheme 2 Proposed mechanism for oxidation of benzyl alcohol with TBHP catalyzed by dioxomolybdenum(VI) Schiff base complex

(entries 7–9, Table 4). The catalytic oxidation can also be successfully performed with sterically hindered alcohols such as diphenylmethanol (entry 10, Table 4).

Based on experimental results and related literature [30-34], a plausible mechanism for oxidation of benzyl alcohol with *tert*-BuOOH (70 % aqueous solution) catalyzed by dioxomolybdenum(VI) Schiff base complex is proposed in Scheme 2.

The first step of the catalytic cycle involves transfer of a TBHP proton to one of the terminal oxygen atoms of  $MoO_2$  group and coordination of *tert*-BuOO<sup>-</sup> to the Lewis-acidic metal center, leading to the formation of the peroxo intermediate in the first step. Then, the peroxo intermediate species oxidizes benzyl alcohol to release one *tert*-BuOH molecule and give an intermediate that leads to benzyl alcohol and H<sub>2</sub>O and regenerates the dioxomolybdenum(VI) Schiff base complex.

#### Conclusions

The catalytic activity of a dioxomolybdenum(VI) Schiff base complex in the selective oxidation of alcohols to aldehydes and ketones with *tert*-BuOOH as oxidant under solvent-free conditions is explored. Easy preparation, mild reaction

condition, good to high yields of products, and ecofriendliness can be mentioned as advantages of this method for oxidizing alcohols.

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#### References

- A. Köckritz, M. Sebek, A. Dittmar, J. Radnik, A. Brückner, U. Bentrup, M.M. Pohl, H. Hugl, W. Mägerlein, J. Mol. Catal. A 246, 85 (2006)
- 2. S. Zhang, L. Xu, M.L. Trudell, Synthesis 11, 1757 (2005)
- 3. J.N. Moorthy, N. Singhal, P. Venkatakrishnan, Tetrahedron Lett. 45, 5419 (2004)
- 4. J.D. Lou, Z.N. Xu, Tetrahedron Lett. 43, 8843 (2002)
- 5. L. Xu, M.L. Trudell, Tetrahedron Lett. 44, 2553 (2003)
- Y.Z. Hou, X.T. Ji, G. Liu, J.Y. Tang, J. Zheng, Y. Liu, W.X. Zhang, M.J. Jia, Catal. Commun. 10, 1459 (2009)
- T. Orbegozo, I. Lavandera, W.M.F. Fabian, B. Mautner, J.G. de Vries, W. Kroutil, Tetrahedron 65, 6805 (2009)
- 8. A.R. Hajipour, I. Mohammadpoor-Baltork, G. Kianfar, Bull. Chem. Soc. Jpn. 71, 2655 (1998)
- 9. S.V. Ley, A. Madin, in *Comprehensive Organic Synthesis*, ed. by B.M. Trost, I. Fleming (Pergamon, Oxford, 1991), p. 251
- 10. M. Beller, Adv. Synth. Catal. 346, 107 (2004)
- 11. X. Li, R. Cao, Q. Lin, Catal. Commun. 69, 5 (2015)
- 12. W. Wang, T. Vanderbeeken, D. Agustin, R. Poli, Catal. Commun. 63, 26 (2015)
- 13. T. Kaicharla, S.R. Yetra, T. Roy, A.T. Biju, Green Chem. 15, 1608 (2013)
- 14. L.Y. Zhu, Z. Lou, J. Lin, W. Zheng, C. Zhang, J.D. Lou, Res. Chem. Intermed. 39, 4287 (2013)
- 15. J. Kamalraja, P.T. Perumal, Tetrahedron Lett. 55, 3561 (2014)
- 16. M.M. Farahani, F. Farzaneh, M. Ghandi, Catal. Commun. 8, 6 (2007)
- 17. M.M. Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 248, 53 (2006)
- K. Ambroziak, R. Pelech, E. Milchert, T. Dziembowska, Z. Rozwadowski, J. Mol. Catal. A: Chem. 211, 9 (2004)
- 19. S.N. Rao, A.K. Kathale, N.N. Rao, K.N. Munshi, Inorg. Chim. Acta 360, 4010 (2007)
- F.E. Kuhn, A.D. Lopez, A.M. Santos, E. Herdweck, J.J. Haider, C.C. Romao, A.G. Santos, J. Mol. Catal. A: Chem. 151, 147 (2000)
- M. Bagherzadeh, M. Amini, H. Parastar, M. Jalili-Heravi, A. Ellern, L.K. Woo, Inorg. Chem. Commun. 20, 86 (2012)
- M. Bagherzadeh, M.M. Haghdoost, A. Ghanbarpour, M. Amini, H.R. Khavasi, E. Payab, A. Ellern, L.K. Woo, Inorg. Chim. Acta 411, 61 (2014)
- 23. Y.D. Li, X.K. Fu, B.W. Gong, X.C. Zou, X.B. Tu, J.X. Chen, J. Mol. Catal. A: Chem. 322, 55 (2010)
- 24. Y. Yang, Y. Zhang, S.J. Hao, Q.B. Kan, J. Colloid Interface Sci. 362, 157 (2001)
- S.M. Bruno, J.A. Fernandes, L.S. Martins, I.S. Goncalves, M. Pillinger, P. Ribeiro-Claro, J. Rocha, A.A. Valente, Catal. Today 114, 263 (2006)
- 26. C.Y. Lorber, S.P. Smidt, J.A. Osborn, Eur. J. Inorg. Chem. 4, 655 (2000)
- 27. M. Hatefi, I. Sheikhshoaie, V. Mirkhani, M. Moghadam, R. Kia, Acta Cryst. E 66, 1137 (2010)
- 28. L.S. Gonzalez, K.S. Nagaraja, Polyhedron 6, 1635 (1987)
- 29. B. Gao, M. Wan, J. Men, Y. Zhang, Appl. Catal. A 439-440, 156 (2012)
- 30. M. Bagherzadeh, L. Tahsini, R. Latifi, K. Woo, Inorg. Chim. Acta 362, 3698 (2009)
- 31. J. Hu, Y. Zou, J. Liu, J. Sun, X. Yang, Q. Kan, J. Guan, Res. Chem. Intermed. 41, 5703 (2015)
- 32. W.R. Thiel, J. Eppinger, Chem. Eur. J. 3, 696 (1997)
- 33. S.M. Bruno, C.C.L. Pereira, M.S. Balula, M. Nolasco, A.A. Valente, A. Hazell, M. Pillinger, P.R. Claro, I.S. Goncalves, J. Mol. Catal. A: Chem. 261, 79 (2007)
- 34. M. Groarke, I.S. Goncalves, W.A. Herrmann, F.E. Kuhn, J. Organomet. Chem. 649, 108 (2002)