

## Paramagnetic Mononuclear Oxovanadium(IV) Complex as Oxidation Catalyst

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Received: 28 September 2017;

Accepted: 31 January 2018;

Published online: 29 March 2018;

AJC-18822

2-Thiophenecarbanicotinic hydrazone is added with equimolar mixture of vanadyl acetyl acetonate in methanol to obtain oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone. Oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone is acted as an effective catalyst in the process. The catalytic reactions were carried under room temperature. The products generated were benzil and furil. The influence of solvent, oxidant and quantity of catalyst has been investigated. Oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone proves significantly higher catalytic activity towards oxidation of secondary alcohols to ketones. The catalyst was proved to be very effective due to its recovery by simple filtration after completion of the reaction. It was reused several times which suggests that there is no change in the catalytic efficiency. Oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone did not show any leaching during the reaction, confirmed the heterogeneous nature.

**Keywords:** Oxovanadium(IV) complex, 2-Thiophenecarbanicotinic hydrazone, Catalytic activity, Oxidation reactions.

### INTRODUCTION

Depending on tautomerism, hydrazones exhibits chelating behaviour. According to the number and type of the substituents in the hydrazone framework, the coordination mode gets influenced. The linkage of hydrazone to a metal ion depends on many factors which includes tautomerism, reaction conditions, stability of the complex formed, number and nature of the substituents on the hydrazone skeleton [1-3]. Metal complexes containing acid hydrazones are found to serve as catalysts in several organic transformation reactions such as polymerization, epoxidation, reduction, oxidation, alkylation and condensation. Tahseen *et al.* [4] have found the catalytic abilities of oxovanadium complexes with hydrazones. They proposed that the complexes are very effective in the conversion of benzoin to benzil. One of the characteristic attribute of oxovanadium is the possibility to tune the electronic and steric properties of complexes. Hydrazones on coordination to metal center through the iminol form facilitates the conjugation and enhances the nonlinearity [5,6]. Cariati *et al.* [7] and Naseema *et al.* [8] have studied the second order non-linear optical parameters of copper and palladium complexes of N-salicylidene-N'-aroylhydrazines. They have proposed the third order non-linear optical properties of some hydrazones derived from *p*-tolylxyacetohydrazide and have observed that the compounds exhibit optical limited behaviour.

Oxovanadium complexes are found to be effective catalysts. As potential catalysts oxovanadium complexes can influence the yields of products and selectivity in many reactions [9,10]. Due to their catalytic efficiencies, oxovanadium complexes have been commonly utilized as precatalysts for epoxidation reactions. Vanadium catalyzed oxidation reactions has attracted several chemists because of the selectivity, reactivity and stereo-selectivity [11]. The catalyst showed high stability, reactivity, and efficiency under various reaction conditions and solvents. The catalysts can be recycled and reused without showing much metal leaching.

### EXPERIMENTAL

2-Thiophene carboxaldehyde, nicotinic hydrazide, benzil, furil, methanol, glacial acetic acid, vanadyl acetylacetonate and acetone were procured from Sigma Aldrich and used without further purification. <sup>1</sup>H NMR spectra were recorded on Bruker AMX 400 FT-NMR spectrometer with DMSO-*d*<sub>6</sub> as solvent and TMS as internal standard.

**Preparation of heterogeneous catalyst 2-thiophenecarbanicotinic hydrazone oxovanadium(IV):** To a solution of 2-thiophenecarbanicotinic hydrazone (0.23 g, 1 mmol) in methanol (20 mL), vanadyl acetylacetonate (0.27 g, 1 mmol) dissolved in methanol (20 mL) was added. The reaction mixture was stirred at room temperature with a magnetic stirrer

for 5 h. The resulting solution was allowed to stand at room temperature for slow evaporation, a precipitated greenish brown coloured solid was separated out. It was washed with methanol and dried under vacuo. Yield: 75 %.

## RESULTS AND DISCUSSION

Physical data of the reactants and synthesized products are summarized in Table-1.

TABLE-1  
PHYSICAL PROPERTIES OF THE  
REACTANTS AND OXIDIZED PRODUCTS

Compound	m.f.	Colour	m.p. (°C)
Benzoin	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	White	134-138
Benzil	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub>	Pale yellow	99

### Catalytic activity

**Oxidation of benzoin and furoin:** Benzoin (0.42 g, 2 mmol) or furoin (0.38 g, 2 mmol) was taken in a round bottom flask (10 mL) and added acetone (5 mL), 2-thiophenecarbanicotinic hydrazonato oxovanadium(IV) (0.1 mmol) as catalyst and  $\text{KMnO}_4$  (0.38 g, 0.5 mmol) or urea- $\text{H}_2\text{O}_2$  adduct (0.38 g, 4 mmol) as the oxidant. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by using TLC. After completion of the reaction the product was purified by column chromatography. The resulting solution was allowed to stand at room temperature for slow evaporation until a yellow coloured crystals formed. The product was washed with water, methanol and ethyl acetate and recrystallized from the solvent used. The product was characterized by  $^1\text{H}$  NMR (Figs. 1 and 2). Oxidation of benzoin gave benzil (**Scheme-I**) while furoin oxidized to furil (**Scheme-II**). The NMR spectra of benzoin (Fig. 1) and benzil (Fig. 2) have revealed that OH signal observed at  $\delta$  6.0 ppm in the former has disappeared in the latter implying that oxidation has taken place. The proton NMR spectra of furoin (Fig. 3) and furil (Fig. 4) have displayed that hydroxyl resonance at  $\delta$  5.9 observed in the former has been disappeared in the latter suggesting that oxidation process has occurred.

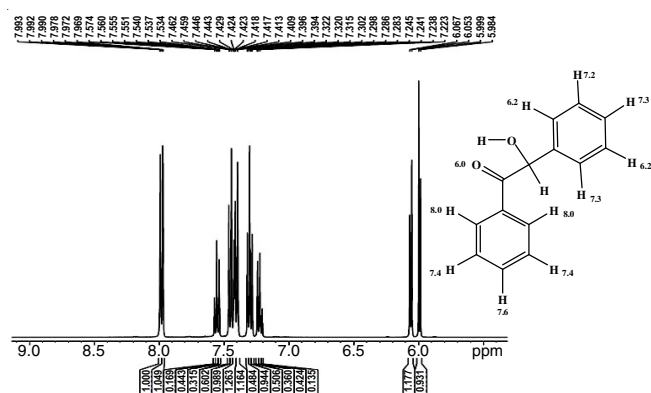


Fig. 1.  $^1\text{H}$  NMR spectrum of benzoin (reactant) in  $\text{DMSO}-d_6$ .

**Recycling of the catalyst:** The catalyst used in the first cycle of the reaction was washed with water, ethyl acetate, and acetone and dried under vacuum and reused again as catalyst.

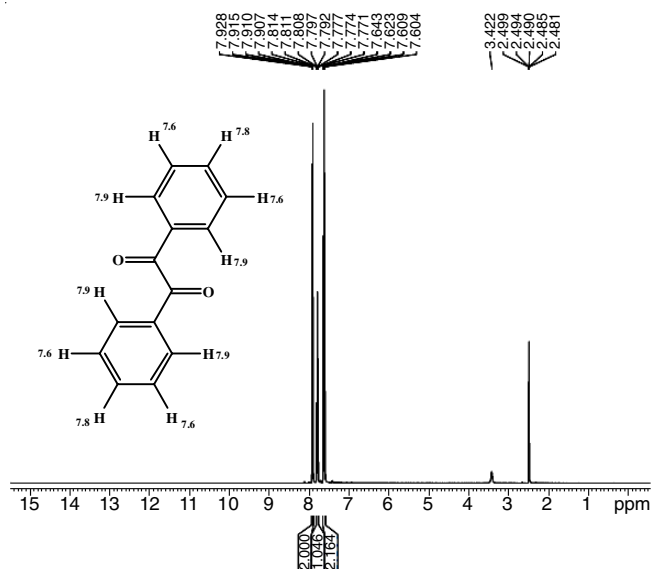
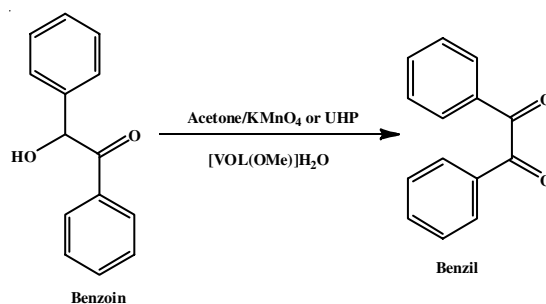
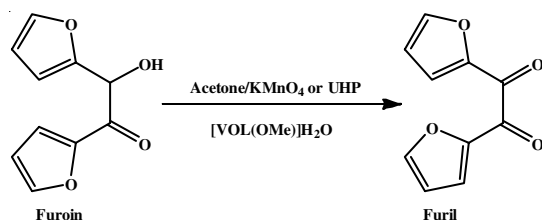


Fig .2.  $^1\text{H}$  NMR spectrum of benzil (product) in  $\text{DMSO}-d_6$



**Scheme-I:** Catalytic oxidation of benzoin to benzil



**Scheme-II:** Catalytic oxidation of furoin to furil

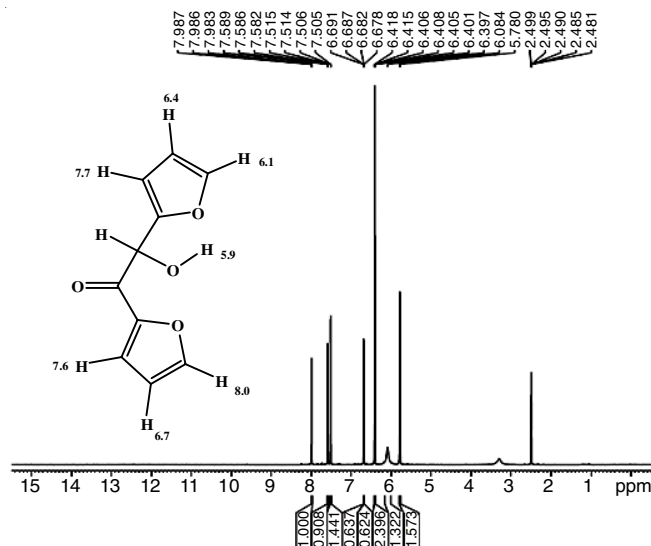


Fig .3.  $^1\text{H}$  NMR spectrum of furoin (reactant) in  $\text{DMSO}-d_6$

TABLE-3  
EFFECT OF SOLVENT IN THE OXIDATION OF ALCOHOLS

Compounds		Acetone		Acetonitrile		Benzene	
Reactant	Product	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
Benzoin	Benzil	3	94	6	85	8	78
Furoin	Furil	2.5	95	6	82	8	80

Reaction conditions: 2 mmol alcohol, 0.5 mmol  $\text{KMnO}_4$ , 5 mL solvent and 0.1mmol catalyst  $[\text{VOL}(\text{OMe})]\text{H}_2\text{O}$ , room temperature

TABLE-4  
EFFECT OF QUANTITY OF THE CATALYST IN THE OXIDATION OF ALCOHOLS

Compounds		0.01 mmol		0.1 mmol		0.15 mmol	
Reactant	Product	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)
Benzoin	Benzil	89	3	94	3	95	3
Furoin	Furil	89	2.5	95	2.5	96	2.5

Reaction conditions: 2 mmol alcohol, 0.5 mmol  $\text{KMnO}_4$ , 5 mL acetone solvent and catalyst  $[\text{VOL}(\text{OMe})]\text{H}_2\text{O}$ , room temperature

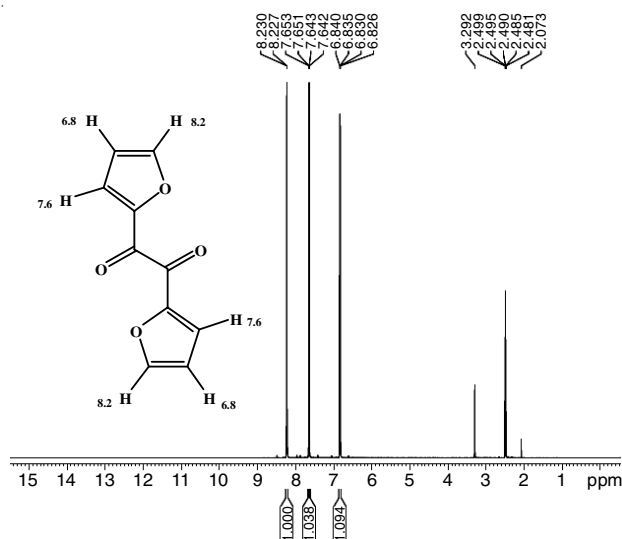


Fig. 4.  $^1\text{H}$  NMR spectrum of furil (product) in  $\text{DMSO}-d_6$

**Effect of oxidant:** In the present case,  $\text{KMnO}_4$  or urea- $\text{H}_2\text{O}_2$  adduct was added as oxidants at room temperature (Table-2). By comparing the efficiency of these two oxidants,  $\text{KMnO}_4$  was observed to be more effective than urea- $\text{H}_2\text{O}_2$ .

TABLE-2  
EFFECT OF OXIDANT IN THE OXIDATION OF ALCOHOLS

Compound		$\text{KMnO}_4$		Urea- $\text{H}_2\text{O}_2$ adduct	
Reactant	Product	Yield (%)	Time (h)	Yield (%)	Time (h)
Benzoin	Benzil	95	3	90	12
Furoin	Furil	98	2.5	89	10

**Effect of solvent on oxidation of alcohols:** In order to study the effect of solvents, the reactions were performed in acetone, acetonitrile and benzene. By comparing the efficiency of the three solvents used, acetone was found to be more suitable than the others (Table-3). It was further observed that the relative conversion in the presence of acetone as solvent was better than the other two solvents. It was also observed that the conversion did not proceed in the absence of solvent.

**Effect of quantity of catalyst on oxidation of alcohols:** The effect of varying quantity of the catalyst on oxidation was also studied. At room temperature, the amount of catalyst was varied from 0.01 mmol to 0.15 mmol keeping the solvent

volume, quantities of oxidant and substrates constant in oxidation reactions. It was observed that 0.1 mmol of catalyst was found to be appropriate (Table-4).

## Conclusion

The catalytic efficiency of oxovanadium(IV) complex of 2-thiophenecarbanicotinic hydrazone, the oxidation of benzoin and furoin were carried out. The experiments were conducted in the presence of 0.01, 0.10 and 0.15 mmol catalyst in three different solvents at room temperature. The rate of the reaction with  $\text{KMnO}_4$  was found to be better than urea- $\text{H}_2\text{O}_2$  adduct and no other side products were formed. The advantage of using oxidants  $\text{KMnO}_4$  or urea- $\text{H}_2\text{O}_2$  adduct was that both could be removed from the reaction mixture easily by washing with water and the catalyst could be reused. The catalyst continued to be active for repeated cycles. There was no appreciable decrease in the activity of 2-thiophene-carbanicotinic hydrazone oxovanadium(IV) catalyst upto five cycles.

## ACKNOWLEDGEMENTS

The author is grateful to Christ University, Bangalore, India for a support. Also acknowledge to Sophisticated Analytical Instrumentation Facility, IISc Bangalore, India for NMR analysis.

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