1008 Chinese Chemical Letters Vol. 14, No. 10, pp 1008 –1011, 2003
http://www.imm.ac.cn/journal/ccl.html

# Asymmetric Dihydroxylation of Allylamine Catalyzed by Wool-$OsO_4$ Complex

Ju Hong MIAO[1]*, Ji Huo YANG[1], Li Yi CHEN[2],
Mei Yu HUANG[2], Ying Yan JIANG[2]

[1] Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074
[2] 4060 group, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080

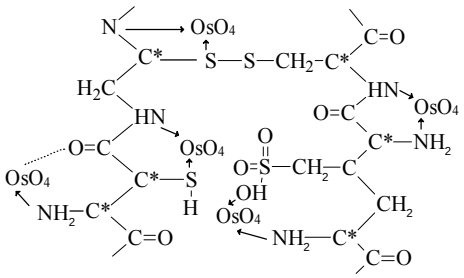
**Abstract:** A new chiral polymer-metal complex, wool-osmium tetroxide(wool-$OsO_4$) complex was prepared by a very simple method. This complex was found to be able to catalyze the asymmetric dihydroxylation of allylamine to get (R)-(+)-3-amino-1, 2-propanediol. The experimental results showed that $OsO_4$ content in the complex, reaction time, allylamine/$OsO_4$ molar ratio all have great effects on the chemical and optical yields of product. Additionally, wool-$OsO_4$ complex catalyst could be reused without remarkable change in optical catalytic activity.

**Keywords:** Wool-osmium tetroxide, asymmetric dihydroxylation, allylamine.

The catalytic *cis*-dihydroxylation of olefinic substrates with $OsO_4$ complex catalyst in the presence of external chiral ligands, represents an important method of obtaining chiral diols[1-3]. It was reported that (R)-(+)-3-amino-1, 2-propanediol[4, 5] was obtained by conventional resolution of the (±)-compounds, which was not an economical method.

In our previous paper[6], a natural biopolymer derivative, chitosan (CS), was used as a ligand of $OsO_4$ complex, and this complex was found to catalyze the asymmetric dihydroxylation of some olefins effectively. Recently, another natural biopolymer, wool, has been used to prepare the wool-$OsO_4$ complex (**Scheme 1**).

**Scheme 1** The chemical structure of wool-$OsO_4$ complex

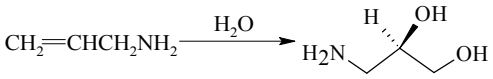



Wool-$OsO_4$ complex has been found to catalyze the asymmetric dihydroxylation of

* E-mail: miaojh_2008@163.com

allylamine to get (R)-(+)-3-amino-1, 2-propanediol. The reaction has been carried out in the presence of $K_3Fe(CN)_6$, $K_2CO_3$, *t*-BuOH, and water at room temperature and under an atmospheric pressure(**Scheme 2**).

**Scheme 2** Asymmetric dihydroxylation of allylamine




## Experimental

*Preparation of wool-osmium tetroxide complex (Wool-$OsO_4$)*

A solution of $OsO_4$ was prepared by dissolving $OsO_4$ (0.5 g) in reagent-grade *tert*-butyl alcohol (100 mL) followed by addition of several drops of 70% *t*-BuOOH. Each milliliter solution should contain $OsO_4$ 5 mg (0.0194 mmol).

Common commercial white wool was washed with water and ethanol, then cut into very small pieces.

Several samples of wool-$OsO_4$ complex with different $OsO_4$ content were prepared by the reaction of a definite amount of wool pieces with $OsO_4$ in *tert*-butyl alcohol solution. The mixture was stirred and heated slowly to 60 $^oC$ for 24 hours under nitrogen atmosphere. After filtration, the solid was washed with *t*-BuOH and dried to obtain wool-$OsO_4$ complex.

*General procedure for the asymmetric dihydroxylation of allylamine*

To a solution of allylamine (2 mmol) in *tert*-butyl alcohol (10 mL) and water (10mL) were added $K_3Fe(CN)_6$ (1.320 g, 4 mmol), $K_2CO_3$ (0.55 g, 4 mmol), and wool-$OsO_4$ (0.32 g, $OsO_4$ content, 0.0588 mmol/g). The reaction mixture was stirred for 24 h at room temperature (about 20 $^oC$). Solid sodium sulfite ($Na_2SO_3$, 1.5 g) was added, and the mixture was stirred for an additional several hours. After filtration, the pale blue solution obtained was concentrated under reduced pressure, and the residue was extracted with three portions of ethyl acetate. The combined extracts were dried over anhydrous magnesium sulfate. This solution was measured by polarimeters, then concentrated under reduced pressure and analyzed by gas chromatography.

## Results and Discussion

The influences of $OsO_4$ content in the complex catalyst, reaction time and allylamine/$OsO_4$ molar ratio on the asymmetric dihydroxylation of allylamine were shown in **Table 1**, **Table 2**, **Table 3**, respectively.

The results summarized in **Table 1**, indicated that the product and optical yields were greatly affected by the $OsO_4$ content in the complex. When the content was 0.0588 mmol/g, the best result was obtained.

**Table 2** showed the influence of reaction time on the asymmetric dihydroxylation of allylamine. It can be seen that the product and optical yields were greatly affected by the reaction time. With the reaction time increasing from 9 to 48 h, the product yield

increased from 57.0 to 90.3%, but the optical yields decreased from 86.5 to 24.2%. Consequently, the best reaction time should be 24 h.

**Table 1** Effect of $OsO_4$ content in complex catalyst

| $OsO_4$ content (mmol/g) | Yield (%) | $[\alpha]_D^{20}$ | Optical yield (%e.e.) | Absolute config. |
|---|---|---|---|---|
| 0.0098 | 66.5 | +12.8 | 45.7 | R |
| 0.0294 | 72.8 | +19.8 | 69.5 | R |
| 0.0588 | 80.2 | +23.4 | 83.7 | R |
| 0.0784 | 82.9 | +14.2 | 50.6 | R |
| 0.0980 | 68.7 | +10.9 | 38.9 | R |

Conditions: catalyst, wool-$OsO_4$, 0.32 g; allylamine, 2 mmol; $K_3Fe(CN)_6$, 1.32 g; $K_2CO_3$, 0.55 g; *t*-BuOH, 10 mL; $H_2O$, 10 mL; 20 °C, 24 h.

**Table 2** Effect of reaction time

| Reaction time (h) | Yield (%) | $[\alpha]_D^{20}$ | Optical yield (%e.e.) | Absolute config. |
|---|---|---|---|---|
| 9 | 57.0 | +24.2 | 86.5 | R |
| 18 | 65.6 | +23.8 | 84.9 | R |
| 24 | 80.2 | +23.4 | 83.7 | R |
| 32 | 85.4 | +12.2 | 43.6 | R |
| 48 | 90.3 | +6.80 | 24.2 | R |

Conditions: catalyst, wool-$OsO_4$ ($OsO_4$ content, 0.0588 mmol/g), 0.32 g; allylamine/$OsO_4$ molar ratio, 100:1; $K_3Fe(CN)_6$, 1.32 g; $K_2CO_3$, 0.55 g; *t*-BuOH, 10 mL; $H_2O$, 10mL; 20 °C.

**Table 3** Effect of allylamine/$OsO_4$ molar ratio

| Allylamine/$OsO_4$ molar ratio | Yield (%) | $[\alpha]_D^{20}$ | Optical yield (%e.e.) | Absolute config. |
|---|---|---|---|---|
| 50:1 | 76.5 | +12.7 | 45.4 | R |
| 100:1 | 80.2 | +23.4 | 83.7 | R |
| 150:1 | 51.2 | +20.4 | 72.8 | R |
| 200:1 | 26.5 | +19.5 | 69.7 | R |

Conditions: catalyst, wool-$OsO_4$ ($OsO_4$ content, 0.0588 mmol/g), 0.32 g; $K_3Fe(CN)_6$, 1.32 g; $K_2CO_3$, 0.55 g; *t*-BuOH, 10 mL; $H_2O$, 10 mL; 20 °C, 24 h.

**Table 4** Reusing ability of catalyst

| Number of used times of catalyst | Yield (%) | $[\alpha]_D^{20}$ | Optical yield (%e.e.) | Absolute config. |
|---|---|---|---|---|
| 1 | 80.2 | +23.4 | 83.7 | R |
| 2 | 80.5 | +23.2 | 82.9 | R |
| 3 | 80.0 | +23.0 | 82.1 | R |

Conditions: catalyst, wool-$OsO_4$ ($OsO_4$ content, 0.0588 mmol/g), 0.32 g; allylamine/$OsO_4$ molar ratio, 100:1; $K_3Fe(CN)_6$, 1.32 g; $K_3CO_3$, 0.55 g; *t*-BuOH, 10 mL; $H_2O$, 10 mL; 20 °C,24 h.

**Table 3** showed the influence of the allylamine/$OsO_4$ molar ratio on the reaction. It can be seen that when the allylamine/$OsO_4$ molar ratio increased from 50:1 to 100:1,

the product yield increased from 76.5 to 80.2% and the optical yield increased from 45.4 to 83.7%. But the further increase of allylamine/$OsO_4$ molar ratio to 200:1, the product and optical yields both decreased to 26.5 and 69.7% respectively.

The catalytic stability of wool-$OsO_4$ on asymmetric dihydroxylation of allylamine was also studied. The results were shown in **Table 4**. It can be seen that after 3-times use of the wool-$OsO_4$ complex, the chemical yield and the optical yield of the products have no significant changes.

## Conclusion

Wool-$OsO_4$ complex was prepared by a very simple method. This complex was found to be able to catalyze the asymmetric dihydroxylation of allylamine to get (R)-(+)-3-amino-1,2-propanediol. The optical and product yields amounted to 83.7 and 80.2%, respectively. Furthermore, wool-$OsO_4$ complex is stable and can be reused without any remarkable change in the optical activity.

## References

1. E. N. Jacobsen, I. Marko, *et al*., *J. Am. Chem. Soc*., **1988**, *110*, 1968.
2. M. Minato, K. Yamamoto, J. Tsuji, *J.Org.Chem*., **1990**, *55*,766.
3. K. B. Sharpless, *et al*., *J.Org.Chem*., **1991**,*56*, 4585.
4. Klieger, Erich, *Ger. Patent*., 2,943,404 1981.
5. Pitre, Daride, Fedeli, Franco, *Arch Pharm*., **1986**, *319* (3), 193.
6. K. Huang, H. W. Liu, D. Xi, M. Y. Huang, Y. Y. Jiang, *Polym. Adv. Technol*., in press.

Received 28 October, 2002