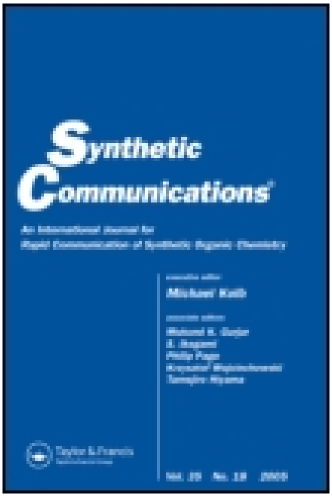


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# A New Methodology for Synthesis of 1,2-Epoxy Alkane with the Linear Aliphatic Olefins in Presence of Molecular Oxygen

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# A NEW METHODOLOGY FOR SYNTHESIS OF 1,2-EPOXY ALKANE WITH THE LINEAR ALIPHATIC OLEFINS IN PRESENCE OF MOLECULAR OXYGEN



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ABSTRACTS: The linear aliphatic olefins, such as 1-octene, 1-decene, 1-dodecene and 1-tetradecene, were effectively epoxidized with molecular oxygen catalyzed by the amino acid Schiff base manganese complex (Sal-Phe-Mn). The products of the reaction was 1,2-epoxy alkane.

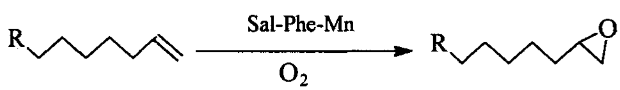
## Introduction

One of the major current challenges in synthetic organic chemistry is the partial, i.e., selective oxidation of organic compounds using molecular oxygen in the presence of transition metal catalysts.[1] Epoxides are one of the most useful synthetic intermediates for the preparation of oxygen-containing natural products or the production of epoxy resins, etc. Much effort has been made to develop the direct and selective epoxidation reaction of olefins by use of molecular oxygen.[2] A few epoxidation reactions of long-chain linear aliphatic olefins with $O_2$ combining transition metal complexes with reducing agents have recently been studied; for example, bis(1,3-diketonato)-nickel complex/isovalveraldehyde.[3] However, the reducing agents will make cost price increasing or make oxides to be easily decomposed. Here, we present the results concerning the aerobic epoxidation of linear aliphatic olefins using Schiff base complexes(Sal-Phe-Mn), which were synthesized by phenylalanine and salicylaldehyde[4]. It is a new methodology for synthesis of 1,2-epoxy alkane with the linear aliphatic olefins in presence of molecular oxygen.



## Result and Discussion

The linear aliphatic olefins **1**, such as 1-octene, 1-decene, 1-dodecene and 1-tetradecene, can be directly epoxidized by molecular oxygen without any reductants or solvents, which afford the 1,2-epoxy alkane.




R = $CH_3$, n-$C_3H_7$, n-$C_5H_{11}$, n-$C_7H_{15}$

The products in catalytic epoxidation of 1-octene(**I**) and 1-decene(**II**) by molecular oxygen were characterized by the system of gas chromatograph with mass spectra, and the products in catalytic epoxidation of 1-dodecene(**III**) and 1-tetradecene(**IV**) by molecular oxygen were characterized by the system of gas chromatograph with IR spectra. Comparing with the data base of the standard Mass Spectra and the standard IR Spectra of Organic Compounds by computer, the products of epoxidation were determined as 1,2-epoxy octane(**I**) 1,2-epoxy decene(**II**), 1,2-epoxy dodecene(**III**), and 1,2-epoxy tetradecene(**IV**), respectively.

**Table 1**. Sal-Phe-Mn catalyzed aerobic epoxidation of linear aliphatic olefins

| Substrate | Time(h) | Conv.(%) | Product |
|---|---|---|---|
|  | 11.5 | 64.6 |  |
|  | 12.5 | 45.9 |  |
|  | 12.0 | 64.0 |  |
|  | 10.0* | 69.3 |  |

Condition: Reaction Temperature: 100 °C ; * 120 °C

Table 1 shows the data abtained on the aerobic epoxidation of linear aliphatic olefins catalyzed by Sal-Phe-Mn. The long-chain linear aliphatic olefins(1-$C_8H_{16}$, 1-$C_{10}H_{20}$, 1-$C_{12}H_{24}$, 1-$C_{14}H_{28}$,) were smoothly epoxidized, but 1-hexene had been evaporated to dryness before it was oxidized by oxygen at 60 °C. The induced period for 1-$C_{12}H_{24}$ was three hours and for 1-$C_{14}H_{28}$ was four hours.

The epoxidation of 1-octene, 1-decene, 1-dodecene or 1-tetradecene did not happen when the reaction temperature was lower than 80 °C, 90 °C, 95 °C or 100 °C, respectively. In most common solvents, such as alcohol, acetonitrile, methylene dichloride and cyclohexane, the epoxidation did not occur because the boiling temperature of the solvents is lower than 80 °C.

In summary, the advantage of Sal-Phe-Mn is easily prepared and no using reductants in epoxidation of long-chain linear aliphatic olefins. They are environmentally more attractive than oxidation based on stoichiometric amounts of $H_2O_2$, ROOH, $NaIO_4$, $Pb(OAc)_4$, $RuO_4$, NaClO or $KMnO_4$.

## Experimental

*Materials and Equipment*

Olefins was purified by fractionating distillation just before use. All other reagents, such as ethyl alcohol, metals salts were of the highest grade commercially available and were used as received.

The metal contents were analyzed on a model ARL-3520 Inductively Coupled Plasmas Atomic Emission Spectrometry of USA. XPS (small area x-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System, Power Source By $MgK_{\alpha}$ line and Ag $3d_{5/2}$ FWHM≤0.48 eV. IR spectra were recorded an Alpha-centauri FT-IR spectrophotometer and Bio-Rad 65A FTS IR system. The mass spectra were measured with Shimadzu QP-1000A GC/MS system.

The amino acid Schiff base manganese complexes (Sal-Phe-Mn) was synthesized by phenylalanine, NaOH, salicylaldehyde and then the solution of $Mn(OAc)_2 \cdot 4H_2O$ in the alcohol[4]. The ligand (Sal-Phe) and its complex (Sal-Phe-Mn) were characterization by IR spectra, and elemental analysis, which confirmed to the formula of Sal-Phe-Mn ($C_{16}H_{13}NO_3Mn \cdot H_2O$, Mn =16.17%).

### 2.2 *Typical Epoxidation procedure:*

A glass flask is charged with Sal-Phe-Mn and olefins. The dry oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The gas outlet tube was closed. The reactor was put into heating bath which temperature was 100 °C, and stirring was started. After reacting for 12 hr, the products was analyzed by gas chromatograph. The structure of products were characterized by Mass spectra and IR spectra.

2.3 *Spectral data for compoumds* **(I-IV)**:

MS, m/z for 1,2-epoxy octane(**I**): 129 (M+1), 128($M^+$, $C_8H_{16}O^+$), 113 ($M^+$-$CH_3$), 99($M^+$-$C_2H_5$), 85($M^+$-$C_2H_3O$ or $M^+$-$C_3H_7$), 70($M^+$-$C_3H_6O$). m/z for 1,2-epoxy decene(**II**): 156($M^+$, $C_{10}H_{20}O^+$), 141 ($M^+$-$CH_3$), 127($M^+$-$C_2H_5$), 113($M^+$-$C_2H_3O$ or $M^+$-$C_3H_7$), 98($M^+$-$C_3H_6O$).

IR data for 1,2-epoxy dodecene(**III**): 3030 $cm^{-1}$($\nu_{OC\text{-}H}$), 2940 $cm^{-1}$; 2850 $cm^{-1}$ ($\nu$C-H), 1460 $cm^{-1}$( $\delta$C-H), 1250 $cm^{-1}$(band 8$\mu$ for 1,2-epoxy alkane), 850 $cm^{-1}$ (band 11$\mu$ for 1,2-epoxy alkane). IR data for 1,2-epoxy tetradecene(**IV**): 3030 $cm^{-1}$ ($\nu_{OC\text{-}H}$), 2940 $cm^{-1}$; 2850 $cm^{-1}$ ($\nu$C-H), 1460 $cm^{-1}$( $\delta$C-H), 1250 $cm^{-1}$(band 8$\mu$ for 1,2-epoxy alkane), 850 $cm^{-1}$ (band 11$\mu$ for 1,2-epoxy alkane).



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