

## CHAPTER IV

### CONCLUSION

The goal of this research is to search for the optimum conditions for metal Schiff's base-catalyzed epoxidation of cyclohexene. The developed catalytic system was also tried to apply to the epoxidation of alkenes derived from natural products. From this research, it was found that the epoxidation of cyclohexene catalyzed by Cr(III) salen.NO<sub>3</sub> with dioxygen in the presence of aldehyde and using acetonitrile as a solvent could be carried out at room temperature with high selectivity for the production of cyclohexene oxide. The optimum conditions disclosed were alkene 5 mmol as a substrate, acetonitrile 30 mL as a solvent, Cr(III) salen.NO<sub>3</sub> 0.2 mmol as a catalyst and 10 mmol of 2-ethylbutyraldehyde or 20 mmol of isobutyraldehyde in the presence of dioxygen as an oxidant. The kinetic study showed that the half-life of cyclohexene epoxidation utilizing this optimum conditions was approximately 6 hours and the reaction was finished within 24 hours.

Comparing with other metal-Schiff's base complexes developed for alkene epoxidation reported in literatures, to our best knowledge this is the first time to disclose the utilization of Cr(III) salen.NO<sub>3</sub> as a catalyst for this type of reaction. In addition, this developed system was clearly shown to provide high yield and high selectivity of the production of the desired product. The outcome from the study of chromium Schiff's base complexes formed *in situ* revealed that the catalytic activity obtained from the *in situ* catalyst was less than that of the synthesized ones. However, the variation of various Schiff's base ligands provided an interesting clues. *Bis* (pyridinyl)-*N, N'*-phenylenediimine and *bis* (2-thiophenealdehyde) *N, N'*-ethylenediimine were found to be the appropriate ligands to generate chromium catalysts *in situ* and provided

moderate yield of products. In addition, the study on the reactivity of Cr(III) salen.NO<sub>3</sub> and Co(II) salen as catalyst was compared and it was disclosed that Cr(III) salen.NO<sub>3</sub> could catalyze the epoxidation reaction slower than Co(II) salen. Furthermore, chemoselectivity study indicated that under this optimum conditions the epoxidation of alkenes was prevailed over the oxidation of alcohol.

The application of this developed epoxidation reaction to other alkenes was also achieved. Cyclooctene and 1-dodecene produced the corresponding epoxides as predominant products. Styrene and  $\alpha$ -methylstyrene were converted to benzaldehyde and acetophenone as major product, respectively. From this results, it was indicated that this system could, in addition, cleave a terminal double bond as that observed in an ozonolysis reaction.

Alkenes from natural products namely,  $\alpha$ - and  $\gamma$ -terpinenes, were studied and found that both of them were cleanly transformed to *p*-cymene. (+)-Valencene was epoxidized to 1, 10-valencene oxide in moderate yield. When pterocarpol which possessed both exocyclic and endocyclic double bonds was used as a chemical probe, it was found that the exocyclic double bond was cleaved and oxidized to the corresponding ketone.

### **Proposal for the Future Work**

There are many interesting points that could be further carried out based upon the outcome originated from this research. For instance, it was found that the ligands around metal were quite essential for the epoxidation reaction. Therefore, the design of the ligands coordinated around metal which will serve as potential catalysts would be a challenging topic to be explored. In addition, the stereoselectivity of this system is crucially needed to be evaluated. An asymmetric epoxidation utilized Cr-Schiff's base complexes should also be performed.

The results obtained from asymmetric synthesis would provide an excellent opportunity to comprehend not only academic aspects on the mechanistic pathway of the reaction, but also the application of the developed reaction to synthesize precious compounds that possessed certain biological activity.

Based upon tremendous attention devoted to the area of selective epoxidation of alkenes<sup>1</sup>, the development of more selective and more practical chemical models to serve in metal-catalyzed epoxidation of alkenes will certainly continue.