

## CHAPTER IV

### CONCLUSION

During the course of this research, the search for another appropriate catalytic system for epoxide ring opening including optimum conditions was thoroughly explored.

Initially, various transition metal salts and transition metal complexes, *i.e.*, metal Schiff's base and metal carboxylate complexes were screened. For some metal salts such as anhydrous  $\text{FeCl}_3$ , the epoxide ring opening could efficiently be occurred in good yield. Other metal salts did not exhibit impressive activity. Metal Schiff's base complexes, especially  $\text{Cr}(\text{salen})\text{Cl}$  could be employed as a potent catalyst for this purpose and gave the desired product in high yield. Nevertheless the drawback of using this class of catalyst was a long reaction time required. For metal carboxylate complexes, some such as  $\text{Fe}(\text{2,4-dinitrobenzoate})_3$ ,  $\text{Fe}(\text{benzoate})_3$ ,  $\text{Fe}(\text{4-nitrobenzoate})_3$  and  $\text{Fe}(\text{TCA})_3 \cdot 1.5\text{H}_2\text{O}$  to our best knowledge had never been utilized as a catalyst in epoxide ring opening reaction. Among them,  $\text{Fe}(\text{TCA})_3 \cdot 1.5\text{H}_2\text{O}$  was disclosed to be the most efficient catalyst for this regard. The reaction could be performed at room temperature for 10 min yield 2-methoxy-2-phenylethanol almost quantitative yield. Indeed this catalyst has not been reported in chemical literature to use for any organic transformation. Thus, the development of a catalytic system utilizing  $\text{Fe}(\text{TCA})_3 \cdot 1.5\text{H}_2\text{O}$  for epoxide ring opening was mainly concentrated.

Styrene oxide was first employed as a chemical model for the opening reaction using methanol as a nucleophile. The reaction could be performed at room temperature and was completed within 10 min. With this catalyst and an enantiopure compound, (*R*)-styrene oxide in this study, an asymmetric ring opening reaction was taken place with 76.51 %*ee*.

Four types of nucleophiles including oxygen, nitrogen, sulfur and halogen nucleophiles were explored in this catalytic system. This catalyst provided good to excellent results with oxygen nucleophiles, particularly when using alcohol as

a nucleophile in the absence of any extra solvent. The yield of the desired product could be increased if the reaction conditions were a bit altered for instance increasing temperature or the amount of catalyst. For nitrogen nucleophile, especially amines, this catalytic system could not provide good results since the amines added rendered the activity (Lewis acid property) of the catalyst used. Nonetheless,  $\text{Fe}(\text{TCA})_3 \cdot 1.5\text{H}_2\text{O}$  catalyzed the epoxide ring opening in the presence of azide to yield the desired product in high yield. For sulfur nucleophile, this catalyst could assist the epoxide opening reaction without difficulty, but less efficient than  $\text{Cr}(\text{salen})\text{Cl}$ . The epoxide ring opening with chlorine ion could be possible; however the yield of the desired product was still low. Some parameters which affected the efficiency of the reaction were need to be modified.

The mechanism of ring opening reaction catalyzed by this complex was clearly demonstrated to take place *via*  $\text{S}_{\text{N}}-1$  reaction. This catalyst was first coordinated with an oxygen atom of epoxide to induce partial positive charge species. Then a nucleophile could attack the epoxide ring at that site to furnish the desired products.

The reactivity of epoxide ring opening was clearly seen from the competitive study among epoxides selected. Styrene oxide reacted with a nucleophile very fast because of the resonance effect from a benzene ring while 1-dodecene oxide required more time or more vigorous conditions.

#### **Suggestion for the future work**

Asymmetric epoxidation utilizing  $\text{Fe}(\text{TCA})_3 \cdot 1.5\text{H}_2\text{O}$  as a catalyst should be conducted. Other types of nucleophiles as well as more epoxide substrates should be tried to extend the scope of this work. More transition metal complexes possessing strong Lewis acid properties, such as Bi, Nb and In should also be investigated. In addition, it was observed that in the absence of good nucleophile, the rearrangement of epoxide was predominant. This reaction should be seriously explored since various chemicals could be produced by this route of reaction.