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EPOXIDATION OF ALKENES CATALYZED BY METAL PORPHYRIN COMPLEXES

Miss Sukanya Jiamworanunkul

A Thesis Submitted in Partial Fulfillment of the Requirements
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ได้ศึกษาปฏิกิริยาเอพอกซิเดชันของแอลคีนโดยใช้แอลดีไฮด์/ออกซิเจนเป็นตัวออกซิไดซ์และสารประกอบเชิงซ้อนโลหะพอร์ไฟรินเป็นตัวเร่งปฏิกิริยา จากการทดสอบความสามารถในการเป็นตัวเร่งปฏิกิริยาเอพอกซิเดชันของไซโคลเฮกซีนของสารประกอบเชิงซ้อนโลหะพอร์ไฟริน ปริมาณและความเลือกจำเพาะในการเกิดเอพอกไซด์ที่ได้ชี้ให้เห็นว่า (*meso*-tetrakis-4-chlorophenylporphyrinato)manganese(III) เป็นตัวเร่งปฏิกิริยาที่มีศักยภาพสูงสุด นอกจากนี้ได้ศึกษาผลของชนิดและปริมาณแอลดีไฮด์ ชนิดตัวทำละลาย ปริมาณแอลคีนและตัวเร่งปฏิกิริยาต่อปฏิกิริยาเอพอกซิเดชัน ภายใต้ภาวะที่เหมาะสม ไซโคลเฮกซีนเปลี่ยนรูปไปเป็นไซโคลเฮกซีนออกไซด์ได้อย่างเลือกจำเพาะในปริมาณสูง 85 เปอร์เซ็นต์ ระบบตัวเร่งปฏิกิริยายังได้มีการพัฒนาขึ้นเพื่อใช้สำหรับปฏิกิริยาเอพอกซิเดชันของแอลคีนชนิดอื่น และพบว่าได้ปริมาณและความเลือกจำเพาะในการเกิดเอพอกไซด์ที่ดีสำหรับปฏิกิริยาเอพอกซิเดชันของสไตรีนและแม้แต่แอลิเฟติกเทอร์มินัลแอลคีน 1-โดเดกซีน ภายใต้ภาวะที่ไม่รุนแรง

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หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา

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The epoxidation of alkenes by aldehyde/oxygen oxidant using metalloporphyrin as catalyst was studied. The catalytic activity of a series of metalloporphyrins was investigated by utilizing the epoxidation reaction of cyclohexene as test reaction. The productivity and selectivity of cyclohexene oxide over the catalysts revealed that (*meso*-tetrakis-4-chlorophenylporphyrinato)manganese(III) acted as the highest potential catalyst. The parameters affected the epoxidation reaction including type and amount of aldehyde, type of solvent and amounts of alkene and catalyst were examined. Under this condition, cyclohexene was selectively transformed to cyclohexene oxide in the maximum yield, ca. 85 %. In addition, the epoxidation system was developed for other epoxide productions. The good yield and selectivity of their corresponding epoxides were obtained from the epoxidations of styrene and even the aliphatic terminal alkene like 1-dodecene under mild conditions.

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LIST OF ABBREVIATIONS

ANAC	*bis*(anthranilic acid) acetylacetone
AACEN	*bis*(acetoacetanitrile) ethylenediamine
ANAAN	*bis*(anthranilic acid) acetoacetanilide
ACDAP	*bis*(acetylacetone) diaminopropane
ACEN	*bis*(acetylacetone) ethylenediamine
4-BrTPP	*meso*-tetrakis(4-bromophenyl)porphyrin
3-ClTPP	*meso*-tetrakis(3-chlorophenyl)porphyrin
4-ClTPP	*meso*-tetrakis(4-chlorophenyl)porphyrin
4-CNTPP	*meso*-tetrakis(4-cyanophenyl)porphyrin
DMA	dimethylacetamide
DMSO	dimethylsulfoxide
HMPT	hexamethylphosphotriamide
PA	2-pyridinecarboxaldehyde
PhIO	iodosylbenzene
ppd	*p*-phenylenediamine
m-CPBA	*m*-chloroperbenzoic acid
mmol	milimole
mL	mililitre (s)
mpd	*m*-phenylenediamine
NMO	*N*-methylmorporline-*N*-oxide
3.4.5-OCH$_3$TPP	*meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrin
4-OCH$_3$TPP	*meso*-tetrakis(4-methoxyphenyl)porphyrin
PTTPP	*meso*-tetrakis(*p*-tolyl)porphyrin
SALEN	*bis*(salicyladehyde) ethylenediamine
SALPA	*bis*(salicylaldehyde) propylenediamine
TMP	*meso*-tetramesitylphenylporphyrin
TPP	*meso*-tetraphenylporphyrin

CHAPTER I

INTRODUCTION AND BACKGROUND

1.1 Introduction

Hydrocarbons naturally abound particularly in petroleum sources. Besides as fuel, these compounds can be used as raw material and changed into more valuable derivatives by chemical reactions. One of important reactions employed is epoxidation yielding epoxides, important intermediates in petrochemical industries.

Selective epoxidation reactions catalyzed by homogeneous catalysts are of industrial significance, especially for the bulk of epoxide productions. Many investigations have been developed for appropiate and viable catalysts on selective epoxidation for over 20 years. Most of catalysts that used for the selective epoxidation are fallen into the utilization of transition metal complex catalysts.

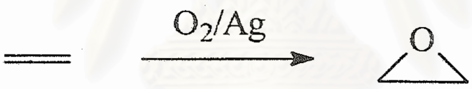
Work during the last decade has laid down the basis for biomimic epoxidation catalysis. Metalloporphyrins have been one of choices and widely used for selective epoxidation of various alkenes because of their structure and ability. These complexes are synthesized to mimic the active site of the metalloenzymes able to oxidize hydrocarbons under mild conditions such as cytochrome P-450 and peroxidase.[1]

Most of oxidants used in the catalytic metalloporphyrin based systems for the epoxidation of olefins in liquid phase were alkyl hydroperoxides, amine *N*-oxides, hydrogen peroxide, iodosylarenes, iodosylbenzene, *m*-chloroperoxybenzoic acid and other peroxy acids, oxiziridines, periodates, potassium monopersulfate and sodium hypochlorite.[2] However, there is no paper dealt with the system employing aldehydes and oxygen which appeared as efficient oxidant in the epoxidation of alkenes catalyzed by such manganese(III) complexes containing 1,3-diketonato ligands or cobalt(II), iron(II), nickel(II) and manganese(III) complexes of 1,3-dioxo, beta-ketoimine or salen types[3] and the epoxidation of alkenes and oxidation of alkanes to the corresponding alcohol and ketone using a combination of copper(II) chloride and crown ether as catalyst.[4] Therefore, the application of this oxidant in the catalytic metalloporphyrin based system for epoxidation of alkenes would be interesting to observe both activity and selectivity of the system.

1.2 Epoxidation of alkenes

Epoxidation is one of the most valuable conversions for petrochemicals. This involves scission of C-C and C-H bonds with formation of C-O bonds. In the other word, alkenes are added with oxygen to carbon double bonds to form epoxides. The cheapest reagent is air. To enhance yield and reaction rate and reduce recycle interval, equipment size and heat loss, oxygen is often employed.[5]

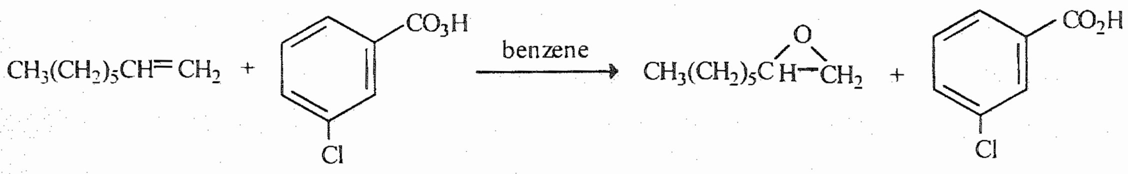
Ethylene oxide, important chemical intermediates is manufactured industrially by direct epoxidation over a hot silver catalyst.[6]



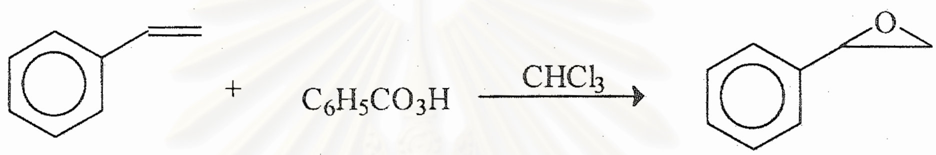
1.2.1 Epoxidation of alkenes with peroxy acids

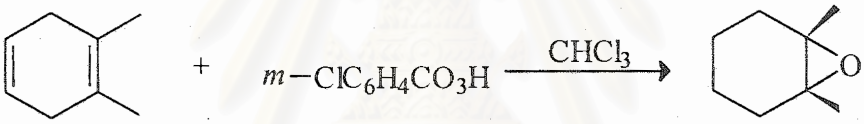
Peroxy acids are the most general reagents for conversion of alkenes to epoxides.

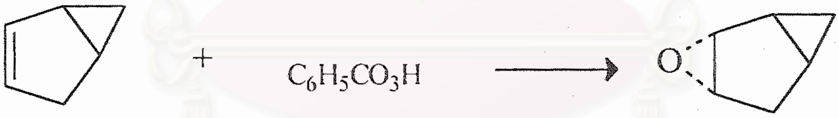
Peroxy acid such as *m*-chloroperbenzoic acid clearly illustrates the redox nature of oxidative addition. Alkenes are epoxidized and *m*-chloroperbenzoic acid is reduced to *m*-chlorobenzoic acid which precipitates slowly from the solution. It has been popular because of its convenient reagent and stable crystalline solid that can be shipped commercially and stored in laboratory. However, *m*-chloroperbenzoic acid, like most other peroxy acids, can be detonated if not handled carefully. Peroxyacetic acid,

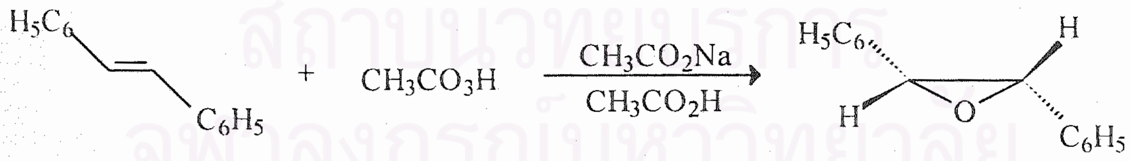


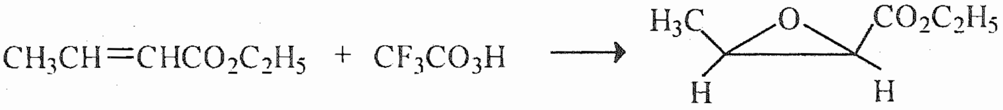
peroxybenzoic acid and peroxytrifluoroacetic acid are also utilized frequently in the epoxidation of alkenes. Peroxyacetic acid, for example, was used in Prilezhaev reaction. A less hazardous peroxy acid with the same activity is the magnesium salt of monoperoxyphthalic acid. Some epoxidations with peroxy acids are shown below.



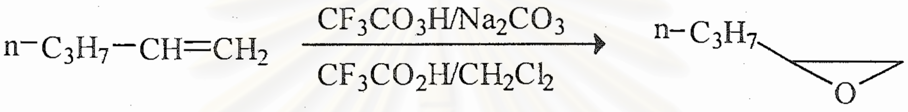




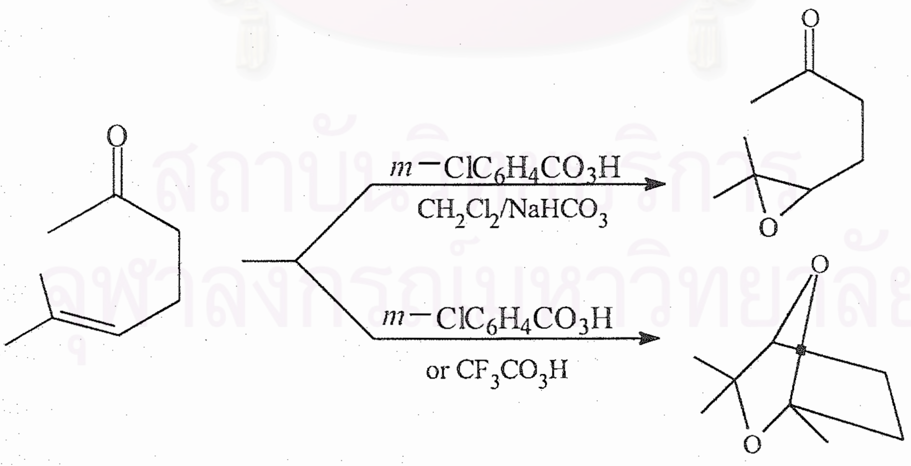




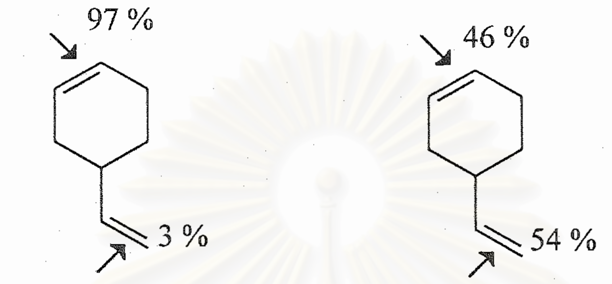
The reaction time usually depends largely on the reactivities of alkene and peroxy acid used. Alkyl groups and other electron-donating substituents on alkene and electron-accepting substituents on peroxy acid increase the reactivities of alkene and peroxy acid.[7] Tri and tetraalkyl alkenes are epoxidized rather quickly even with relatively weak peroxy acids while monosubstituted alkenes require stronger peroxy acids.[8] Unreactive terminal alkenes, for example, *n*-pentene could be converted to epoxide with peroxytrifluoroacetic acid. In this case anhydrous sodium carbonate or disodium hydrogen phosphate must be added to the reaction to neutralize the trifluoroacetic acid produced.[9] Very low reactivity is also exhibited by double bonds that are conjugated with strongly electron-attracting substituents and strongly oxidizing peroxy acids such as trifluoroacetic acid and peroxymalelic acid are required for epoxidations of such compounds.[10]



For acid sensitive alkenes, which usually form rearranged products with aliphatic and aromatic peroxy acids, can conveniently be epoxidized with *m*-chloroperoxybenzoic acid in a dichloromethane-sodium bicarbonate two phase system.[11]

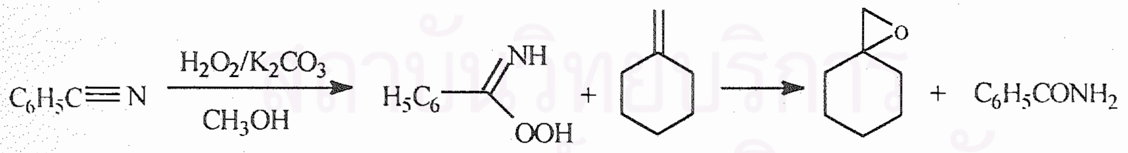


Peroxybenzimidic acid appears to be less sensitive than other peroxy acids for the epoxidation of alkenes. Vinylcyclohexene reacted with *m*-chloroperoxybenzoic acid to give predominantly 1,2-epoxide while peroxybenzimidic acid epoxidized both double bonds to almost the same degree.[12]

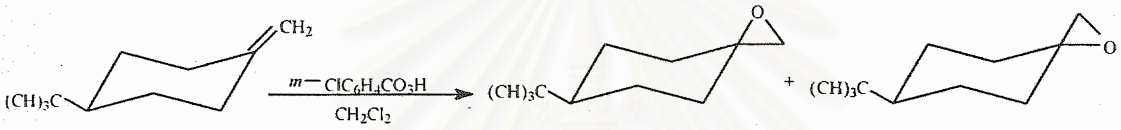


m—ClC$_6$H$_4$CO$_3$H   C$_6$H$_5$C(NH)O$_2$H

The choice of the preferred peroxy acid for epoxidation also depends on the stability of epoxide. Carboxylic acids that are formed in the reaction can react with the epoxide produced to give monoester 1,2-diols especially lower aliphatic acids. Epoxide that are unstable under acidic conditions can be prepared by epoxidation with peroxybenzimidic acid. An effective process involves reaction of an alkene, a nitrile and hydrogen peroxide in a buffer solution at pH 8. The nitrile and hydrogen peroxide react, forming a peroxybenzimidic acid, which epoxidizes the alkene, presumaly by a mechanism similar to that for peroxy acids.[13]

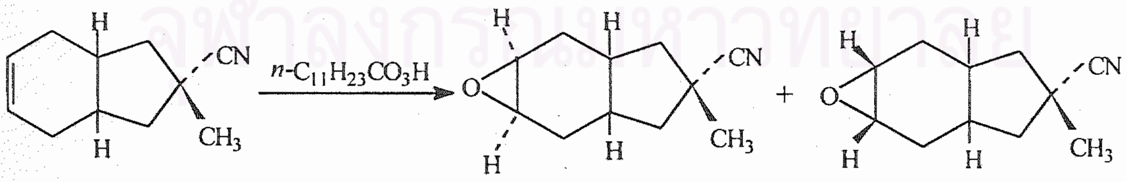


The stereoselectivity of epoxidations with peroxy acids has been well studied. The epoxidations have been demonstrated that ionic intermediates are not involved in the epoxidation reaction. Stereospecific *syn*-addtion is consistantly observed. The epoxidation is therefore believed to be a concerted process. Apparently, neighboring functional groups influence the direction of the attack of the peroxy acid. Addition of oxygen occurs preferentially from the less hindered side of the molecule. Norbornene, for example, epoxidized with *m*-chloroperoxybenzoic acid afforded the exo-epoxide in 99 % yield.[14] Epoxidation of allylic compounds with a bulky group as a neighboring substituent proceeded with a preferential attack. Epoxidation of 3-*tert*-butylcyclohexene with *m*-chloroperoxybenzoic acid in dichloromethane approximately yielded a 9:1 ratio of *trans*- to *cis*-epoxides. In molecules that two potential modes of approach are not greatly different, for instance, the unhindered exocyclic double bond in 4-*t*-butylmethylenecyclohexene gave both stereoisomeric products, *exo*- and *endo*-epoxides in 69 and 31 % yield.[15]

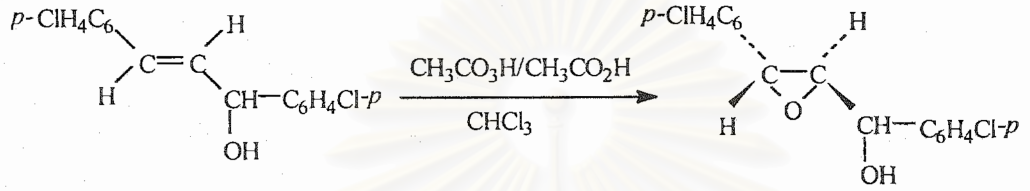


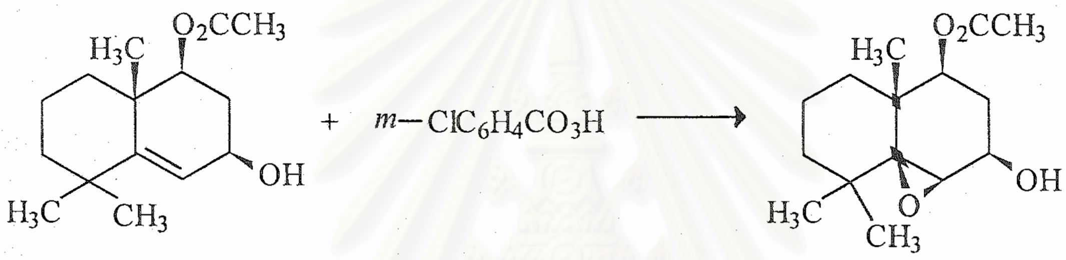
Remote groups can also affect the direction of the approach of the peroxy acid. 4-methylcyclopentene reacted with peroxylauric acid to give 73:27 ratio of *trans*- to *cis*-epoxides. This ratio unchanged significantly on going from nonpolar to polar solvents indicating the alkyl group exerted a steric effect rather than polar effect.[16]

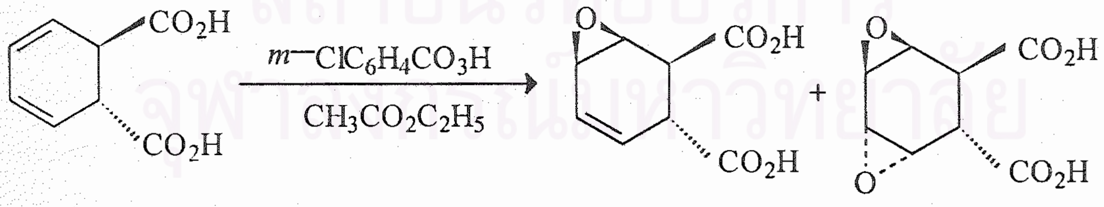
Preference for anti epoxidation has been observed also in systems in which a polar group is too far from the double bond to exhibit any steric influence. This preference disappears in polar solvents indicating that a polar effect must be operative with such groups. For example, epoxidation of the alkene below with peroxylauric acid in cyclopentene gave a 72:28 ratio for *trans*- to *cis*-epoxide and a 55:45 ratio in acetonitrile.[17]

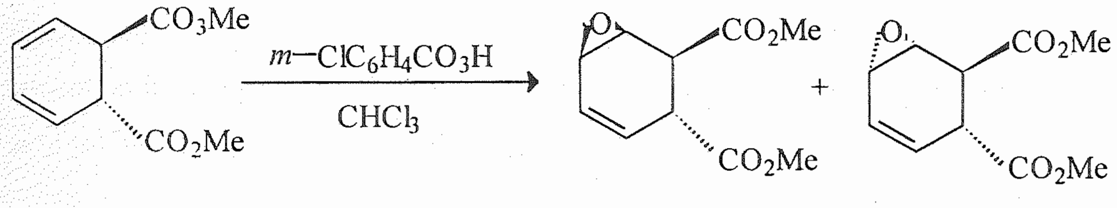


In hydroxyl directive effect, on the other hand, hydroxyl groups in the allylic or homoallylic position exert a strong directive effect on epoxidation and favor approach from the side of the double bond closest to the hydroxyl group. The effect can produce stereochemical control even when steric effects are opposed. Stereospecificity diminishes or disappears, with both *cis*- and *trans*-isomers giving predominantly or exclusively the product which the incoming oxygen is *syn*-addition to the OH group. Hydrogen bonding between the hydroxyl group and the peroxy acid evidently stabilized the transition state.[18] For instance, epoxidation of the allylic alcohol, 2-cyclohexene-1-ol, produced a 9:91 ratio *trans*- to *cis*-epoxides with little dependence on the solvent used.[16] Similar results were reported for unsaturated steroids having a free hydroxyl substituent in the allylic position.[19] Allylic carboxylic acids and carboxylates are also effective *syn*-directing groups. For example, the epoxidation of *trans*-1,2-dihydrophthalic acid gave only the *cis*-monoepoxide while the epoxidation of dimethyl *trans*-1,2-dihydrophthalate yielded 9:1 mixture of *cis*- and *trans*-epoxides.

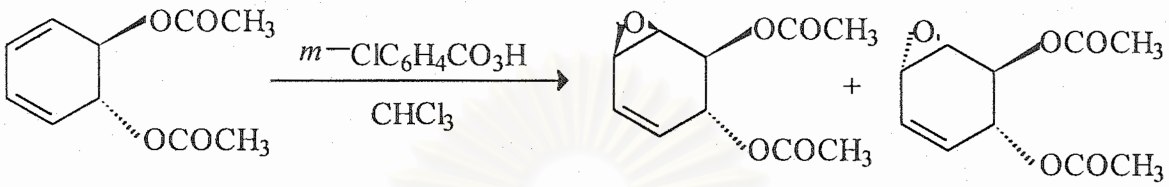








Epoxidation of allylic acetates is considerably less stereospecific as an example shown below. A 2:1 mixture of *cis*- and *trans*-epoxides has been obtained by epoxidizing with peroxybenzoic acid in benzene.[14]



The relative order of *syn*-directing ability of substituents in allylic epoxidation is believed to be OH > CO_2H > CO_2R > OCOR.[20]

Epoxidations with peroxy acids are a second order reaction (first order in alkenes and first order in peroxy acid).

$$v = k[RCO_3H][\text{alkene}]$$

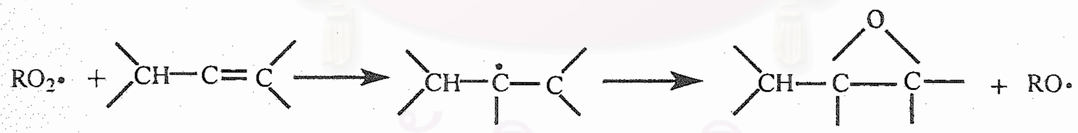
Electron releasing groups in the alkene accelerate the rate of epoxidation and electron-withdrawing groups retard it thus indicating the nucleophilic nature of alkenes in epoxidation. Conjugation of the alkene double bond with phenyl rings reduces the rate of epoxidation. The trend of decreasing reactivity of some representative alkenes with peroxybenzoic acid is styrene > *cis*-stilbene > *trans*-stilbene > triphenylethene > tetraphenylethene.[21] The planar structure of *trans*-stilbene enables the delocalization of electron density of the double bond. Such a delocalization is not possible in *cis*-stilbene owing to the nonplanarity of both rings. As a result, *cis*–stilbene is approximately twice as reactive as *trans*-stilbene. In general, *cis*-double bonds in straight chain alkenes are epoxidized faster than *trans* double bonds and the reverse holds for *cis*–*trans* isomers of medium-size cycloalkenes. The kenetic of epoxidation of strained alkenes indicates that the rate is indepentdent of the strain. For example, 1,2-cyclopentene reacted 11.7 times faster than 1,2-diphenylcyclopropene with *m*-chloroperoxybenzoic acid in carbon tetrachloride. Norbornene reacted 2.4 times faster than cyclohexene with peroxylauric acid in chloroform.[14]

Electron withdrawing groups in the peroxy acid facilitate the rate of epoxiadation. This structure-reactivity relationship demonstrates that the peroxy acid acts as an electrophile in the reaction. The order of reactivity approximates the pK values of the peroxy acids, i.e., peroxytrifluoroacetic > monoperoxymaleic > monoperoxyphthalic > *p*-nitroperbenzoic > *m*-chloroperoxybenzoic > peroxyformic > peroxybenzoic > peroxyacetic acids.[22]

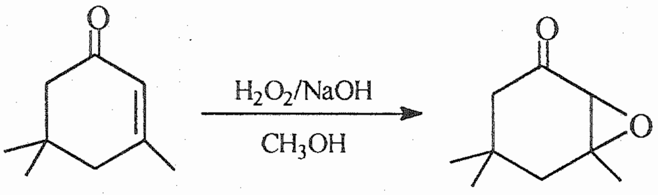
1.2.2 Epoxidation of alkenes with hydroperoxides

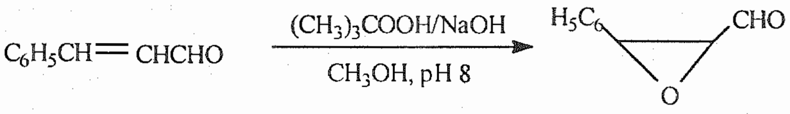
Besides peroxy acids, hydroperoxides are used in epoxidation of alkenes especially, hydrogen peroxide and *tert*-alkyl hydroperoxides. *Tert*-butyl hydroperoxide and cumyl hydroperoxide are available commercially from several sources. The oxidizing power of those compounds is comparable to that of hydrogen peroxide. Alkyl hydroperoxides are stronger acids than the corresponding alcohols. They form salts with aqueous sodium hydroxide which enables their easy separation from the reaction mixture and purification.[23]

Epoxides are produced in the autooxidation of simple alkenes *via* addition of a peroxy radical to the double bond. However, yields are usually low for cyclohexene, cyclopentene and styrene due to other competing reactions.[24]

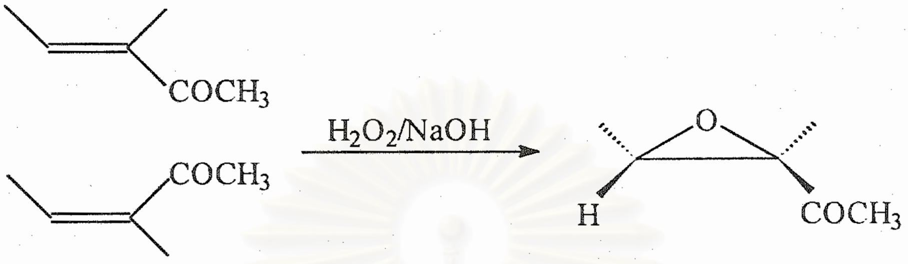


Efficient use of hydroperoxides is selective epoxidations of *α,β*-unsaturated ketones and aldehydes with sodium salt of hydrogen peroxide or sodium salt of *tert*-butylhydroperoxide.[25]





In contrast to epoxidation with peroxy acids, these reactions are selective than stereospecific, for example, only one isomer was obtained by the epoxidation of either isomer of the unsaturated ketone.[26]



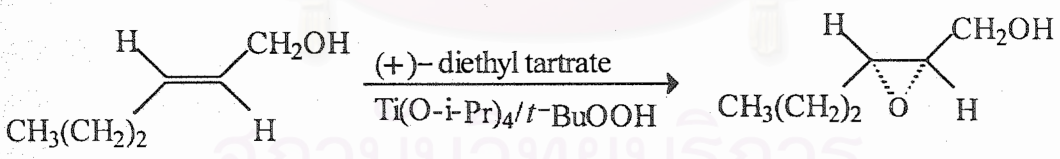
Alkylidenemalonic esters, unsaturated sulfones, unsaturated nitro compounds and vinyl phosphates can also be epoxidized with these reagents.[27]

Other hydroperoxides, like cyclic *α*-azo hydroperoxides are extremely reactive in epoxidation. The machanism of oxygen atom transferred from the hydroperoxides is similar to that of peracids. Intramolecular hydrogen bonding of the hydroperoxide hydrogen and the azo-linkage is apparently important in the transition state for the epoxidation.[28]

1.2.3 Epoxidation of alkenes catalyzed by metal complexes

The epoxidation of new routes toward the selective epoxidation of alkenes is a very active field nowadays. In addition to the industrial importance of this process, the catalytic chemistry has constituted the mainstream of researches in the epoxidation reaction. Many metal complexes have been tested to survey efficient catalysts desired.

Vanadium pentoxide was employed to catalyze epoxidation of alkenes, cyclohexene and 1-octene in the presence of hydrogen peroxide. The yield of epoxides obtained, cyclohexene oxide and 1-octene oxide were 39 and 15 % respectively.[29] Much higher yield of 1-octene, 53 %, was reported by using oil-soluble acetylacetonates of either vanadium or molybdenum as catalyst.[30] Epoxidations catalyzed by the vanadium or molybdenum complexes in the presence of hydroperoxides were found that the epoxide product was invariably one of *cis*-addition to the carbon double bond. Increasing concentration of the catalyst and using high reaction temperature promoted some side reaction, which may be hydrolysis of the epoxide produced.[31] Vanadium oxoacetylacetonate, vanadium naphthenate, vanadium oxide and molybdenum acetylacetonate were published to catalyze the epoxidation of cyclohexene. Efficient epoxidation occured at low oxygen pressure whereas high oxygen pressure yielded ketone.[32] For vanadyl-acetylacetonate-*t*-butyl hydroperoxide in cyclohexene-cyclohexane mixture, *t*-butyl alcohol produced severe retardation, probably by competition with *t*-butyl hydroperoxide for complexing sites. Vanadium pentoxide, tungsten and molybdenum trioxide were claimed as excellent catalyst for the epoxidation of crotyl alcohol yielding 97 % of the epoxide. Refluxing cyclohexene with an equimolar quanity of 90 % *t*-butyl hydroperoxide and a bit of molybdenum naphthenate or trioxide readily converted about half of the cyclohexene to cyclohexene oxide in 2 to 3 hours while reducing 90 to 95 % of the hydroperoxide to *t*-butyl alcohol.[26] In the reaction of molybdenum(VI) peroxy complexes $[Mo(O_2)_2O]L_1L_2$ (L_1 was organic compounds like DMA, DMF and HMPT) with various alkenes, corresponding epoxides are formed in high yield.[33] The enantioselective epoxidation of allylic alcohols such as (+)-diethyl tartrate was highly enantioselective, 97 % e.e. in the system of titanium tetraisopropoxide and *t*-butylhydroperoxide (Sharpless asymmetric epoxidation).[34] Nickel complexes of bidentate heterocyclic amines such as 2,2′-bipyridine and 1,10- phenanthroline acted as active catalyst for the epoxidation of alkenes with hypochlorite as terminal oxidant and epoxides were obtained as major product.[35] The epoxidation of alkenes with an aldehyde and molecular oxygen with a catalytic amount of nickel(II), iron(III), vanadium (IV), and manganese(II) complexes containing 1,3-diketonato ligands was reported. The efficiency of catalysts was improved by designing the structure of the ligands. Alkenes like styrene derivatives and unsaturated carboxamides were oxidized to the corresponding epoxides in high yields. Enantioselective and aerobic epoxidations of unfunctionalized olefins proceeded in good to high enantiomeric excess of optically active epoxides in the presence of a catalytic amount of manganese(III) complexes having optically



active 1,3-diketonato ligands, *N,N-bis*(3-oxobutylidene) diamine derivatives combining use of molecular oxygen and pivalaldehyde. The key intermediates in this aerobic epoxidation were tentatively proposed to be acylperoxomanganese complexes.[36] Mechanism and kinetic of the aerobic epoxidation of alkenes with an aldehyde and substituted *β*-diketonate-transition metal complexes as catalysts were studied. *β*-Diketonate complexes of nickel(II) were proved to be the best catalysts for this reaction. The epoxidation was not dependent on substrate concentration and was first order in aldehyde, catalyst concentration and oxygen partial pressure. This system was believed to occur *via* radical intermedaite by reactivity studies, EPR experiments and stereochemical investigations.[37] Copper salt catalyst like copper(II) hydroxide was reported to have high performance in the epoxidation of alkenes and the oxidation of alkanes to the corresponding alcohols and ketones with an aldehyde and molecular oxygen (1 atm) as oxidant source at room temperature.[4] The epoxidation of alkenes was catalyzed by mixed heteropolyoxometalate $[(NH_4)_5H_4PV_6Mo_6O_{40}$. 6 $H_2O]$ in the presence of 2 equivalent of 2-methylpropanol and oxygen. The corresponding epoxides were obtained as product in moderate to good yields depending on the amount of the catalyst employed.[38] An efficient system for the epoxidation of 1-phenylcyclohexene, whose epoxide was sensitive to acid catalyzed destruction and was difficult to prepare, was found. 1-Phenylcyclohexene oxide was obtained in 91% yield from the reaction catalyzed by methyltrioxorhenium and utilized 30 % hydrogen peroxide as oxidant in the presence of pyridine in dichloromethane at room temperature. Another efficient synthesis of acid sensitive epoxides such as chromene oxide was successfully achieved by the epoxidation of chromene catalyzed by cobalt(II) complex of 1,3-diketone ligand with the combined use of aldoacetal in the presence of molecular oxygen at atmospheric pressure.[39]

Chromium salen Schiff base complexes were reported to efficiently catalyze epoxidation of various alkenes with iodosylbenzene. Chromium(III) salen cation was promoted by pyridine *N*-oxide and related oxygen donors as cocatalyst. The donor adduct $[O{=}Cr(salen)(pyO)\ ]^+$ was believed to be the reactive intermediate in the catalytic cycle. The oxo-product of norbornene oxide could be isolated in 70 % yield.[40]

Iron(III) Schiff base chelates, $[Fe_2(PA_2pd)_2Cl_2]Cl$, $[Fe_2(PA_2ppd)_2Cl_4]Cl_2$ and $[Fe_2(PA_2mpd)_2Cl_4]Cl_2$ were used as catalyst in the epoxidation of norbornene with iodosylbenzene. Norbornene oxide yields obtained were only 2, 6 and 8 % respectively.[41]

Chiral salen (*N,N'-bis*(salicyldeneamono)ethane)manganese(III) was reported as a good catalyst for asymmetric stilbene epoxidation by using sodium hypochlorite as oxidant in air. *Cis*-stilbene could be transformed to *cis*-stilbene oxide in 85 % yield.[42] Manganese(III) Schiff base complexes (Schiff bases were SALEN, ANAC, AACEN, ANAAN, ACDAP, SALPA and ACEN) were employed as catalyst in the epoxidation of alkenes in the presence of PhIO as oxidant. For epoxidation of cyclohexene, cyclohexene oxide, cyclohexenone and cyclohexenol were obtained. The effect of catalyst concentration showed that the yield of the epoxide decreased when increasing the amount of the catalyst. The relative rate of the reaction toward cyclic alkenes followed the order: norbornene > cyclooctene > cycloheptene > cyclohexene > cyclopentene.[43] Manganese complex bearing the optically active salen ligand [*N,N'-bis*(*S*)-3-(1-phenylpropyl) salicylidene]-(1*R*, 2*R*)-1,2-diphenylethylethylenediaminato] was found to be an effective catalyst for the enantioselectivity of 50 % e.e. in the epoxidation reaction of (*E*)-1-phenyl-1-propene. The highest enantioselectivity of 48 % e.e. of (*E*)-stilbene was disclosed by using the chiral salen manganese(III) complexes, [(8*S*, 8'*S*)-3,3'-bis[(1*R*)-1-phenylpropyl]-4,4'-dimethyl-8,8'-diphenylsalen]manganese(III) complex.[44] Chiral manganese salen complexes substituted in the 3 position with bulky silyl groups (TMS or TBDMS) catalyzed the epoxidation of unfunctionalized alkenes giving moderate to high e.e.'s.[45] 1,2-Dihydronaphthalene was efficiently epoxidized with the system of oxygen and isobutyraldehyde or iodosylbenzene in the presence of manganese(III) salen catalyst. The nickel(II), cobalt(II) and iron(III) catalysts of either salen- or beta-ketoimine- types were useful for epoxidation of styrene, (*E*)-stilbene and (*E*)-benzalacetone in the system using oxygen and isobutyraldehyde. This epoxidation system was stereospecific without the formation of the corresponding diastereomeric epoxides.[1] A variety of oxidants was the effective oxygen donor for alkene epoxidations in the precence of chiral salen manganese(III) complexes. The combination of *m*-CPBA and NMO was found to be particularly effective even at low reaction temperature. Epoxidation of a wide array of unfunctionalized alkenes proceeded with an increase in enantioselectivity under anhydrous low temperature conditions relative to biphasic reactions employing bleach. Other alkenes, either water-soluble or decomposable in the presence of aqueous bleach were also viable substrates for the epoxidation reaction.[46] Enantioselective epoxidation of unfunctionalized alkenes was achieved by the combined use of molecular oxygen and pivalaldehyde in the presence of a catalytic amount of optically active manganese(III) salen complexes. *N*-alkylimidazoles were effective axial ligands to produce optically active epoxides with high enantioselectivities, for instance, 1,2-dihydronaphthalene derivatives and 2,2-dialkyl-2H-chromene derivatives were converted into the corresponding optically active epoxides with 60 to 92 % e.e.[47]

Nickel complex, [*N,N'*-*bis*[*o*-(*p*-toluenesulfonylamino)benzylideneethylenediaminoto]nickel(II), was found to be a good catalyst for the epoxidation of alkenes with molecular oxygen in the presence of 2-methylpropanol (Mukaiyama's condition). *Trans*-stilbene gave *trans*-stilbene oxide up to 79 % yield.[48]

For asymmetric epoxidation of styrene catalyzed by chiral ruthenium(II) Schiff bases derived from salicyldehyde and L-amino acids) in the presence of iodosylbenzene, the R form of the catalyst resulted in the formation of (*S*)-styrene oxide as dominant enantiomer.[49] Both $[Ru(Me_3tacn)O_2(CF_3CO_2)]^+$ and *cis*-dioxoruthenium(VI) complex of *N,N'.N''*-trimethyl-1,4,7-triazacyclononane were reported to catalyze alkene epoxidation by PhIO. Cyclohexene gave cyclohexene oxide as major product under the particular condition.[50]

Bis(salicylidene-*N*-phenethyl)] cobalt(II), could catalyze the reaction of aliphatic aldehydes and oxygen with unactivated alkenes leading to the corresponding epoxides, whereas the reactions with electron deficient alkenes afforded the adducts between aldehyde and alkenes.[51]

Apart from the metal complexes above, metalloporphyrin is another interesting group. Metalloporphyrin is a coordination compound of metal and porphyrin. The basic structure of the porphyrin consisted of the porphine structure of four pyrrole rings linked by four methane bridges in a cyclic configuration. Metalloporphyrin provides an extremely versatile synthetic base on which to design physical and chemical properties and its porphyrin ring is very stable to concentrated acid. It performs diverse functions such as oxygen and electron transports and also has a lot of fascinating applications including catalysis.[52]

The past year has witnessed significant advance in the study of epoxidation-catalyzing metalloporphyrin. Metalloporphyrin has been recently reported successes in the epoxidation of alkenes and has become the principal substance used not only to model the chemical and physical properties of oxidative metalloenzymes such as cytochrome P-450 but also to promote catalytic oxygen transfers especially the epoxidation reaction.

Epoxidation of alkenes with iodosylbenzene was catalyzed by (5,10,15,20-tetraphenylporphyrinato)iron(III) chloride. Cyclohexadiene oxide 93 %, cyclooctene oxide 84 % and *cis*-stilbene oxide 77 % were attained. However, *trans*-stilbene was found to be unreactive under this condition.[53] Iron(III) complex of β-hexanitro–*meso*-tetra-2,6-dichlorophenylporphyrin was a remarkable catalyst for the epoxidation of cyclooctene with diluted hydrogen peroxide. Complete conversion of cyclooctene and 97 % yield of cyclooctene oxide were obtained in 0.5 hour.[54] Five *cis*-cycloalkenes with ring sizes, 5, 6, 7, 8 and 10 and a *cis-trans* mixture of cyclododecene were epoxidized by iodosylbenzene using tetra(2,6-dichlorophenylporphyrinato)iron(III) or manganese(III) chloride as catalyst. Both catalysts gave similar product distributions. Epoxides were obtained as major product while allylic oxidation also occurred particularly in case of cyclopentene, cyclohexene and cyclododecene.[55] The epoxidation of 3β-acetoxycholest-5-ene with cumene hydroperoxide was catalyzed by electron-withdrawing and (perchlororinated 5, 10,15,20-tetraarylporphyrinato)iron(II) chlorides. The products obtained were identified as 3β-acetoxy-5α,6α-epoxycholestane, 3β-acetoxy-5β,6β-epoxycholestane, 3β-acetoxy-7α-hydroxycholest-5-ene, 3β-acetoxy-7β-hydroxycholest-5-ene and 3β-acetoxy-7-oxocholest-5-ene in different yields depending on the reaction conditions. Good yield of 5β,6β-epoxides was attained with (2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetraarylporphyrinato)iron(III) chloride as catalyst.[56] Effectively enantioselective epoxidation of unfunctionalized alkenes like styrene, pentafluorostyrene and metachlorostyrene was reported. The epoxidation was carried out at room temperature by using chiral iron porphyrins as catalyst and iodosylbenzene as epoxidizing agent. Also, for nonconjugate terminal alkenes such as 3,3-dimethylbutene and vinyltrimethylsilane, the system gave high enantioselectivity.[57] The epoxidation of alkenes was catalyzed by an electron-rich iron(III) porphyrin complex, (*meso*-tetramesitylporphyrinato)iron(III) chloride, using 30% hydrogen peroxide as oxidant in the presence of 5-chloro-1-methylimidazole in aprotic solvent. Epoxides were the predominant products with trace amounts of allylic oxidation products. In addition, the reactivities of other iron(III) porphyrin complexes such as (*meso*-tetrakis(2,6-dichlorophenyl)porphinato)iron(III) chloride, (*meso*-tetrakis(2,6-difluorophenyl) porphinato)iron(III) chloride, and (*meso*- tetrakis(pentafluorophenyl)porphinato)iron(III) chloride were significantly affected by the presence of imidazole in the epoxidation of alkenes by hydrogen peroxide. These iron porphyrin complexes did not yield cyclohexene oxide in the epoxidation of cyclohexene by hydrogen peroxide in the absence of 5-chloro-1-methylimidazole in aprotic solvent while the addition of 5-chloro-1-methylimidazole to the reaction solutions gave high yields of cyclohexene oxide with the formation of trace amounts of allylic oxidation products. It could be proposed that the role of the imidazole was to decelerate the O-O bond cleavage of an iron(III) hydroperoxide porphyrin adduct and that the intermediate transferred its oxygen to olefins prior to the O-O bond cleavage.[58]

Epoxidation of alkenes by oxygen and zinc as reducing agent was achieved by using (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride in the presence of 1-methylimidazole and acetic acid. Cyclooctene oxide, cyclohexene oxide and 2-methylhept-2-ene oxide were obtained in 50, 49 and 34 % yield respectively. Less substituted double bond of buta-1, 3-diene could be epoxidized with (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride with sodium iodosylbenzene in good yield.[59] Epoxidation of alkenes catalyzed by several manganese porphyrin complexes was carried out by utilizing various oxidants such as iodosylarenes, peracids, alkylhydroperoxides, hydrogen peroxide, amine *N*-oxides, oxaziridines, monopersulfates and perchlorates. In most cases, their transition states were believed to occur *via* hypervalent manganese(IV) oxoporphyrin species which were suggested as the viable oxidant in the catalytic systems.[60] The epoxidation of styrene by sodium periodate was catalyzed by (acetatotetraphenylporphyrinato)manganese(III) in the presence of various polybenzimidazole compounds and tetra-*n*-butylammonium bromide in dichloromethane-water media. Absolute selectivities and high yields, 75-84 % were obtained in 3 hours at ambient temperature.[61] *Cis*-stilbene stereospecifically yielded *cis*-stilbene oxide in the epoxidation employing (5,10,15,20-tetramesitylphenylporphyrinato)manganese(III) chloride as catayst in the presence of imidazole in dichloromethane. The epoxidation rate linearly depended on the catalyst concentration and the epoxidation route could not preceed in the absence of imidazole.[62] Epoxidation of prochiral alkenes with enantiomeric excess in the range 22 to 31 % was reported by using manganese complex of chiral porphyrin prepared by condensation of enantiomerically pure [22.2]-4-*p*-cyclophane-4-carbaldehyde and pyrrole. The reaction was carried out in the presence of aqueous sodium hyperchlorate at pH 10 as oxygen donor and small amount of 4-*tert*-butylpyridine as axial ligand in dichloromethane-water two phase condition.[63] Additive such as Cl-, Br-ions and 1-methylimidazole were added to increase yield of cyclohexene oxide in the epoxidation of cyclohexene in dichloromethane containing (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride as catalyst, insoluble zinc powder as reductant, benzoic anhydride as cleaving reagent of oxygen double bond and hexylviologen as mediator.[64] [5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl) porphyrinato]manganese(III) and [2,3,7,8,12,13,17,18-octachloro-5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrinato]manganese(III) chloride have been synthesized and used as catalyst in alkene epoxidations by iodosylbenzene and hydrogen peroxide. The former catalyst showed higher efficiency because the eight additional chlorine atoms on the porphyrin ring of the latter catalyst stabilized metal center and unflavored the formation of the active spicies.[65] Several manganese(III) porphyrins bearing bispyridyl groups increased turnover numbers for the catalytic epoxidation of styrene upon the addition of bulky Lewis acids such as (5,10,15,20-tetraphenylporphyrinato)-zinc and magnesium. The enhancement was attributed to the formation of a coordination trimer which provided steric protection of the catalyst from bimolecular decomposition. In many cases, the addition of the Lewis acids was reported to the regeneration of deactivated catalysts and full recovery of the catalytic activity.[66]

The aerobic epoxidation of linear terminal alkenes such as 1-octene and propene can be accomplished by Ru(TMP)O_2, as catalyst with turnovers of 40 and 36 respectively during 1 day. The catalytic activity of Ru(TMP)O, after this time nearly completely vanished. The deactivation of catalyst was also studied and proposed that it may result from the formation of a carbonyl species Ru(TMP)CO which the source of CO was the alkene substrate.[67] The oxygen atom transfer reaction from 2,6-disubstituted pyridine *N*-oxides to alkenes was efficiently catalyzed by ruthenium porphyrins. The substrate could be converted into corresponding epoxides with high selectivity. These epoxidations also proceeded with other heteroaromatic *N*-oxides, such as pyrazine *N*-oxides, as oxidants.[68] The epoxidations of styrene and norbornene catalyzed by substituted ruthenium(VI) dioxoporphyrin complexes were studied in the solution of methylene chloride and pyrazole. For using (*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato)ruthenium(VI) and (*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)ruthenium(VI) as catalyst, styrene oxide was obtained in good yield, 91 and 69% respectively. However, cyclohexene oxide was obtained in low yield only 30 and 9 % for epoxidation of cyclohexene by employing these two complexes.[69] In enantioselective epoxidation of unfunctionalized alkenes such as styrene catalyzed by iron, manganese and ruthenium complexes of one particular homochiral porphyrin under various conditions, it was found that the metal catalyst, epoxidizing agent and solvent affected the enantioselectivity of the epoxide product. The best enantioselectivity was obtained when using the iron porphyrin as catalyst, iodosylbenzene or iodosylmesitylene as epoxidizing agent in aromatic solvent like benzene.[70]

1.3 The objective of this research

In this research, the catalytic epoxidation by metalloporphyrin complexes under mild condition will be investigated. The interested oxidant source is a variety of aldehydes and oxygen, which has no report to utilize in the epoxidation system. Epoxidation of cyclohexene to cyclohexene oxide is firstly chosen as model reaction to examine. Application of the knowledge of this will be focused to epoxidations of other types of alkene such as 1-dodecene and styrene. The outcomes of this work will build up the beneficial view of the practical oxidant in the catalytic metalloporphyrin-based epoxidation.

The goal of this study can be summarized as follows:

1. To prepare porphyrin ligands and metalloporphyrin complexes.

2. To study the optimum conditions for the epoxidation of alkenes using the metalloporphyrin complexes as catalyst and aldehydes and oxygen as oxidant under mild conditions.

CHAPTER II

EXPERIMENTAL SECTION

2.1 Instrument

Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 PF 254). The FT-IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410: the solid samples were mixed with potassium bromide to form pellets. The ^{1}H-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as internal reference on a Bruker model AFC 200 Spectrometer. Gas chromatography analysis was carried out on a Shimadzu Gas Chromatography GC-9A and GC-14A instrument equipped with flame ionization detector (FID) with N_2 as carrier gas. The column used for chromatography was a capillary column type of DB-WAX (30 m x 0.25 mm) from J&W Scientific.

2.2 Chemicals

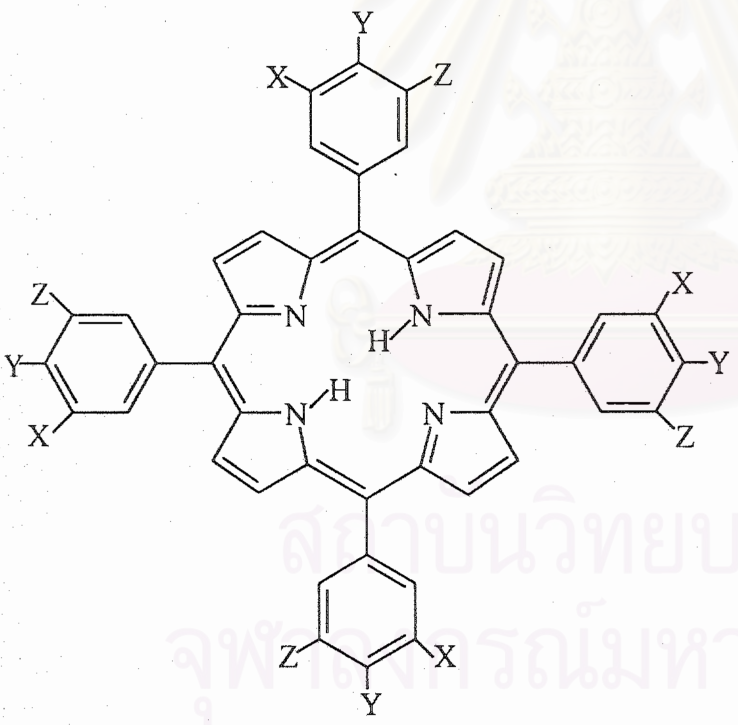
The reagents for synthesizing porphyrin ligands and metalloporphyrin complexes and for utilizing in epoxidation reactions were purchased from Fluka and Merck chemical companies. All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades.

2.3 Syntheses

2.3.1 Porphyrin ligands

2.3.1.1 General procedure[71]

To a solution of freshly distilled pyrrole (0.02 mol-equiv) in propionic acid (75 mL), an interested aldehyde (0.02 mol-equiv) was slowly added. The mixture was refluxed and monitored the progress of the reaction by thin-layer chromatography. The reaction mixture was allowed to cool down to room temperature and then filtered. The precipitate was washed thoroughly with methanol to remove the tarry impurity until the filtrate was clear. The purple crystal product was recrystallized from an appropriate solvent.



(1) X, Y, Z = H

(2) X = Cl Y, Z = H

(3) X, Y, Z = OCH_3

(4) X, Z = H Y = Br

(5) X, Z = H Y = Cl

(6) X, Z = H Y = CN

(7) X, Z = H Y = CH_3

(8) X, Z = H Y = OCH_3

Structures of porphyrin ligands studied

***Meso*-tetraphenylporphyrin** (TPP) **(1):** Bright purple crystal (20 %), R_f 0.49 (dichloromethane: hexene, 2:3). IR (KBr, cm^{-1}) 3330, 3065-3020, 1600, 1178, 970-690; UV-Vis (CH_2Cl_2, nm) 412, 514, 548, 590 and 648; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.86 (8H, s), 8.28 (8H, d, J = 7.0 Hz), 7.77 (8H, t, J = 7.0 Hz) and 7.24 (4H, d, J = 7.0 Hz).

***Meso*-tetrakis(3-chlorophenyl)porphyrin** (3-ClTPP) **(2):** Bright purple crystal (18 %), R_f 0.59 (dichloromethane: hexene, 2:3). IR (KBr, cm^{-1}) 3315, 3140-3060, 1585, 1190, 975-691 and 450; UV-Vis (CH_2Cl_2, nm) 412, 514, 546, 592 and 644.

***Meso*-tetrakis(3,4,5-methoxyphenyl)porphyrin** (3,4,5-OCH_3TPP) **(3):** Bright purple crystal (18 %), R_f 0.79 (ethyl acetate: hexene, 3:2). IR (KBr, cm^{-1}) 3300, 2950-2830, 1585, 1178, 110, 1230 and 1000-715; UV-Vis (CH_2Cl_2, nm) 422, 516, 552, 590 and 648; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.96 (12H, s), 4.18 (24 H, s), 7.47 (8H, s) and 8.96 (8H, s).

***Meso*-tetrakis(4-bromophenyl)porphyrin** (4-BrTPP) **(4):** Bright purple crystal (25 %), R_f 0.73 (dichloromethane: hexene, 2:3). IR (KBr, cm^{-1}) 3310, 3080-3000, 1560, 1178, 1110-700 and 455; UV-Vis (CH_2Cl_2, nm) 418, 512, 550, 588 and 646; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.83 (8H, d, J = 8.0 Hz), 8.05 (8H, d, J = 8.0 Hz) and 8.83 (8H, s).

***Meso*-tetrakis(4-chlorophenyl)porphyrin** (4-ClTPP) **(5):** Bright purple crystal (21 %), R_f 0.58 (dichloromethane: hexene, 2:3). IR (KBr, cm^{-1}) 3310, 3100-3020, 1675, 1178, 970-690 and 495; UV-Vis (CH_2Cl_2, nm) 418, 514, 548, 588 and 646; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.74 (8H, d, J = 6.67 Hz), 8.11 (8H, d, J = 6.67 Hz) and 8.83 (8H, s).

***Meso*-tetrakis(4-cyanophenyl)porphyrin** (4-CNTPP) **(6):** Purple crystal (19 %), R_f 0.29 (dichloromethane: hexene, 4:1). IR (KBr, cm^{-1}) 3300, 3095-3035, 2215, 1610, 1178 and 970-690; UV-Vis (CH_2Cl_2, nm) 414, 514, 548, 590 and 646; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.09 (8H, d, J = 8.0 Hz), 8.32 (8H, d, J = 8.0 Hz) and 8.79 (8H, s).

***Meso*-tetrakis(*p*-tolyl)porphyrin** (PTTPP) **(7):** Bright purple crystal (20 %), R_f 0.37 (dichloromethane: hexene, 4:1). IR (KBr, cm^{-1}) 3315, 3020, 1640, 1460, 1178 and 970-740; UV-Vis (CH_2Cl_2, nm) 472, 528, 584 and 620; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.70 (12H, s) 7.54 (8H, d, J = 8.0 Hz), 8.09 (8H, d, J = 8.0 Hz) and 8.85 (8H, s).

***Meso*-tetrakis(4-methoxyphenyl)porphyrin** (4-OCH_3TPP) **(8):** Bright purple crystal (17 %), R_f 0.11 (dichloromethane: hexene, 3:3). IR (KBr, cm^{-1}) 3310, 3035, 2830, 1610 and 990-730; UV-Vis (CH_2Cl_2, nm) 422, 518, 555, 594 and 649; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.09 (12H, s) 7.28 (8H, d, J = 9.0 Hz), 8.11 (8H, d, J = 9.0 Hz) and 8.85 (8H, s).

2.3.2 Metalloporphyrin complexes

2.3.2.1 General procedure[72]

A porphyrin ligand was dissolved in dimethylformamide. Then, a metal chloride was added to the porphyrin solution. The mixture was refluxed and the reaction was followed by UV Spectroscopy to ensure that the metallation was complete (at this point a visible spectrum of an aliquot taken from the reaction mixture revealed the absence of the porphyrin ligand). The reaction mixture was cooled down to room temperature. After adding cold water, the precipitate was filtered and washed with water.

(*Meso*-tetraphenylporphyrinato)manganese(III) chloride, Mn(III)TPP: Green solid (81 %), IR (KBr, cm^{-1}) 3040-3000, 1590, 1178, 1014-695; UV-Vis (CH_2Cl_2, nm) 401, 478, 583 and 618.

(*Meso*-tetrakis(3-chlorophenyl)porphyrinato)manganese(III) chloride, Mn(III)3-ClTPP: Green solid (83 %), IR (KBr, cm^{-1}) 3060-3020, 1590, 1230, 890-690 and 450; UV-Vis (CH_2Cl_2, nm) 476, 526, 578 and 616.

(*Meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato)manganese(III) chloride, Mn(III)3,4,5-OCH_3TPP: Green solid (84 %), IR (KBr, cm^{-1}) 3040-3000, 2840, 1570, 1240, 1130, 950-650 and 438; UV-Vis (CH_2Cl_2, nm) 482, 530, 583, and 618.

(*Meso*-tetrakis(4-bromophenyl)porphyrinato)manganese(III) chloride, Mn (III)4-BrTPP: Green solid (92 %), IR (KBr, cm^{-1}) 3050-3030, 1585, 1200, 1015-715 and 476; UV-Vis (CH_2Cl_2, nm) 475, 532, 579, and 616.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)cobalt(II),** Co(II)4-ClTPP: Brown-orange solid (97 %), IR (KBr, cm^{-1}) 3095-3015, 1685, 1200, 1010-715 and 497; UV-Vis (CH_2Cl_2, nm) 412 and 528.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)iron(III) chloride,** Fe(III)4-ClTPP: Brown solid (98 %), IR (KBr, cm^{-1}) 3120-3000, 1630, 1198, 1000-720 and 500; UV-Vis (CH_2Cl_2, nm) 415 and 508.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)manganese(III) chloride,** Mn(III)4-ClTPP: Green solid (99 %), IR (KBr, cm^{-1}) 3090-3015, 1660, 1200, 1000-717 and 502; UV-Vis (CH_2Cl_2, nm) 476, 530, 582, and 618.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)nickel(II),** Ni(II)4-ClTPP: Blue solid (61 %), IR (KBr, cm^{-1}) 3105-3025, 1630, 1178, 1000-700 and 502; UV-Vis (CH_2Cl_2, nm) 416 and 428.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)oxovanadium(IV),** VO(IV) 4-ClTPP: Reddish purple solid (72 %), IR (KBr, cm^{-1}) 3095-3010, 1640, 1205, 1010, 890-720 and 500; UV-Vis (CH_2Cl_2, nm) 422 and 546.

***(Meso*-tetrakis(4-chlorophenyl)porphyrinato)zinc(II),** Zn(II)4-ClTPP: Purple solid (50 %), IR (KBr, cm^{-1}) 3100-3020, 1635, 1200, 1000-715 and 490; UV-Vis (CH_2Cl_2, nm) 424 and 550.

***(Meso*-tetrakis(4-cyanophenyl)porphyrinato)manganese(III) chloride,** Mn(III)4-CNTPP: Green solid (87 %), IR (KBr, cm^{-1}) 3120-3040, 2220, 1600, 1200, and 1014-717; UV-Vis (CH_2Cl_2, nm) 472, 526, 577 and 609.

***(Meso*-tetrakis(*p*-tolyl)porphyrinato)manganese(III) chloride,** Mn(III)PTTPP: Green solid (96 %), IR (KBr, cm^{-1}) 3027, 1618, 1500, 1183 and 1014-730; UV-Vis (CH_2Cl_2, nm) 476, 523, 586 and 620.

(*Meso*-tetrakis(4-methoxyphenyl)porphyrinato)manganese(III) chloride, Mn(III)4-OCH_3TPP: Green solid (87 %), IR (KBr, cm^{-1}) 3055, 2820, 1613, 1255, 1178 and 1010-715; UV-Vis (CH_2Cl_2, nm) 478, 533, 584 and 624.

2.4 General procedure for the epoxidation of cyclohexene

A dichloromethane solution (30 mL) composing cyclohexene (5 mmol) and the metalloporphyrin, Mn(III)4-ClTPP (0.1 mmol) in a round bottom flask was fitted with a balloon filled with oxygen. After adding 2-ethylbutyraldehyde (10 mmol), the mixture was stirred for 24 hours at room temperature. The reaction mixture was worked up by extracting with diethyl ether, saturated $NaHCO_3$ and brine, respectively and analyzed by gas chromatography with the addition of an exact amount of an appropriate internal standard. All product yields were based on starting cyclohexene.

2.5 General procedure for the epoxidation of 1-dodecene and styrene

The general procedure was based on the method affiliated to the developed optimun condition of the cyclohexene epoxidation; a acetonitrile solution (30 mL) composing 1-dodecene or styrene (4 mmol) and the metalloporphyrin, Mn(III)4-ClTPP (0.05 mmol) in a round bottom flack was fitted with a balloon filled with oxygen. After adding 2-ethylbutyraldehyde (10 mmol), the mixture was stirred for 4 hours at room temperature. The reaction mixture was worked up by extracting with diethyl ether, saturated $NaHCO_3$ and brine, respectively and analyzed by gas chromatography with the addition of an exact amount of an appropriate internal standard. All product yields were based on the starting alkene.

2.6 Optimum condition study for the epoxidation of cyclohexene

2.6.1 Effect of metalloporphyrin

2.6.1.1 Effect of metal

According to the general procedure, the epoxidation reaction of cyclohexene was carried out by employing six metallo-tetrakis-4-chlorophenylporphyrin complexes, Co(II)4-ClTPP, Fe(III)4-ClTPP, Mn(III)4-ClTPP, Ni(II)4-ClTPP, VO(IV)4-ClTPP and Zn(II)4-ClTPP as catalyst.

2.6.1.2 Effect of porphyrin ligand

The epoxidation reaction of cyclohexene was carried out in the same manner to the general procedure using eight different substituted manganese(III) porphyrin complexes, Mn(III)4-BrTPP, Mn(III)3-ClTPP, Mn(III)4-ClTPP, Mn(III)4-CNTPP, Mn (III)3,4,5-OCH_3TPP, Mn(III)TPP, Mn(III)4-OCH_3TPP and Mn(III)PTTPP as catalyst.

2.6.2 Effect of type of aldehyde

The epoxidation reaction of cyclohexene was carried out according to the general procedure and various aldehydes such as anisaldehyde, benzaldehyde, butyraldehyde, cyclohexanecarboxaldehyde, 2-ethylbutyraldehyde and isobutyraldehyde were utilized.

2.6.3 Effect of solvent

The epoxidation reaction of cyclohexene was carried out in the same fashion to the general procedure and a variety of solvents such as acetonitrile, benzene, chloroform, 1,2-dichloroethane, dichloromethane and metanol were exploited.

2.6.4 Effect of the amount of 2-ethylbutyraldehyde

The epoxidation reaction of cyclohexene was carried out in the similar manner to the general procedure but using acetonitrile as solvent and the amount of 2-ethylbutyraldehyde was varied in the range of 0, 5, 10, 15 and 20 mmol.

2.6.5 Effect of the amount of cyclohexene

The epoxidation reaction of cyclohexene was carried out in the same way to the general procedure but using acetonitrile as solvent and the amount of cyclohexene was changed into 2, 3, 4 and 5 mmol in 4 hrs.

2.6.6 Effect of the amount of catalyst

The epoxidation reaction of cyclohexene was carried out in according to the general procedure but using acetonitrile as solvent and the amount of catalyst, Mn(III)4-ClTPP was switched into 0.025, 0.05, 0.1, 0.15 and 0.2 mmol in 4 hrs.

2.7 Stability study of cyclohexene oxide

The epoxidation reaction was performed in the similar manner to the general procedure but excercising cyclohexene oxide as substrate and acetonitrile as solvent instead of cyclohexene and dichloromethane, respectively. In addition, the reaction handled without the catalyst in the same condition was managed.

2.8 Comparative kinetic study of the epoxidation of cyclohexene catalyzed by various metalloporphyrins

The general procedure for the epoxidation of cyclohexene dealing with five metalloporphyrin complexes, Mn(III)4-ClTPP, Mn(III)TPP, Mn(III)PTTPP, Co(II)4-ClTPP and Fe(III)4-ClTPP as catalyst was conducted. At different reaction time proceeded (1, 2, 4, 8 and 12 hrs), an aliquot (1 mL) from the reaction mixture was taken, worked up and analyzed by gas chromatography.

2.9 Comparative reactivity study of Co(II)-, Fe(III)- and Mn(III)4-ClTPP on the epoxidation of cyclohexene

Co(II)-, Fe(III)- and Mn(III)4-ClTPPP were employed as catalyst in the cyclohexene epoxidation operating with the developed optimum condition of the cyclohexene epoxidation.

2.10 Application of the developed epoxidation reaction

Besides the endocyclic alkene like cyclohexene, another type of alkenes, 1-dodecene and styrene for aliphatic and aromatic terminal alkenes were selected as substrate to broaden epoxidation study by starting with the knowledge of the developed epoxidation of cyclohexene. Consequently, the epoxidations of 1-dodecene and styrene were firstly conducted in the optimum condition of the cyclohexene epoxidation.

2.10.1 The epoxidation of 1-dodecene

2.10.1.1 Effect of amount of substrate on the epoxidation of 1-dodecene

Following to the epoxidation procedure, the epoxidation reaction of 1-dodecene was carried out in the same way while 1-dodecene was used as substrate and the amount of 1-dodecene was altered into 1, 2, and 4 mmol.

2.10.1.2 Effect of reaction time on the epoxidation of 1-dodecene

The epoxidation was performed in the similar manner to the general procedure. At different reaction time proceeded (4, 6, 8, 10 and 12 hrs), an aliquot (1 mL) from the reaction mixture was taken, worked up and analyzed by gas chromatography.

2.10.2 The epoxidation of styrene

2.10.2.1 Effect of amount of substrate on the epoxidation of styrene

In according to the epoxidation procedure, the epoxidation reaction of styrene was accomplished by using styrene as substrate and the amount of styrene was adjusted to 1.5, 2.5, 3.5 and 4 mmol.

CHAPTER III

RESULTS AND DISCUSSION

This research was engrossed in one of fundamentally industrial processes, epoxidation of alkenes, particularly cyclohexene, 1-dodecene and styrene to their corresponding epoxides. Metalloporphyrins were synthesized and employed as catalyst in the epoxidation reaction. A combination of aldehydes and oxygen was selected as oxidant source. To improve the catalytic system, optimum conditions and some interesting aspects of the alkene epoxidation such as kinetic analysis were studied.

3.1 Synthesis and characterization of porphyrin ligands

Eight porphyrin ligands could be prepared by the condensation reaction of pyrrole and appropriate aldehydes according to the literature recipe.[71] Their identities were inspected by UV-Vis, IR, and NMR techniques prior to use for synthesizing the metalloporphyrin complexes. From the UV-Vis spectroscopy, the Soret band of the porphyrin exhibited a peak occurring between 412-472 nm. In addition, IR spectra showed a characteristic absorption band attributed to N-H stretching vibration in the region of 3310-3330 cm^{-1}.[73]

3.2 Synthesis and characterization of metalloporphyrin complexes

Metallation to form all metalloporphyrin complexes was performed by the reaction of the porphyrin ligand with suitable metal chloride in dimethylformamide.[72] Their features were identified by UV-Vis and IR techniques. As the UV-Vis observation, the Soret band of the complexes, generally, slightly shifted in frequency from that of the corresponding porphyrin ligands depended on the metal inserted except for the manganese complexes that represented the marked shift in frequency. Furthermore, the IR spectra straight revealed the disappearance of the N-H stretching vibration band due to the metal insertion.

3.3 Optimum condition study for the epoxidation of cyclohexene

In this work, cyclohexene was the first substrate chosen as a chemical model. There are many factors needed to evaluate to optimize the epoxidation reaction. Some interesting parameters included type and amount of metalloporphyrin (catalyst), type and amount of aldehyde, type of solvent, and amount of cyclohexene (substrate).

3.3.1 Effect of metalloporphyrin

3.3.1.1 Effect of metal

Various metal complexes of one particular porphyrin, *meso*-tetrakis-4-chlorophenylporphyrin, were investigated as catalyst for the cyclohexene epoxidation in order to search for an appropriate metal complex. The catalytic activity and selectivity of the metalloporphyrin observing upon the epoxidation are presented in Table 3.1 and Fig 3.1.

Table 3.1 The epoxidation of cyclohexene catalyzed by metallo-tetra-4-chlorophenylporphyrins

Entry	Metal(4-ClTPP)	Product (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	Epoxide/Enone
1	Co(II)	22.34	4.49	4.98
2	Ni(II)	10.63	1.27	8.37
3	Zn(II)	trace	0	-
4	Fe(III)	28.84	18.36	1.57
5	Mn(III)	52.13	4.14	12.59
6	VO(IV)	22.88	5.30	4.32

Reaction condition: Metal(4-ClTPP) 0.1 mmol, 2-ethylbutyraldehyde 10 mmol, cyclohexene 5 mmol, dichloromethane 30 mL, O_2, room temp and 24 hrs

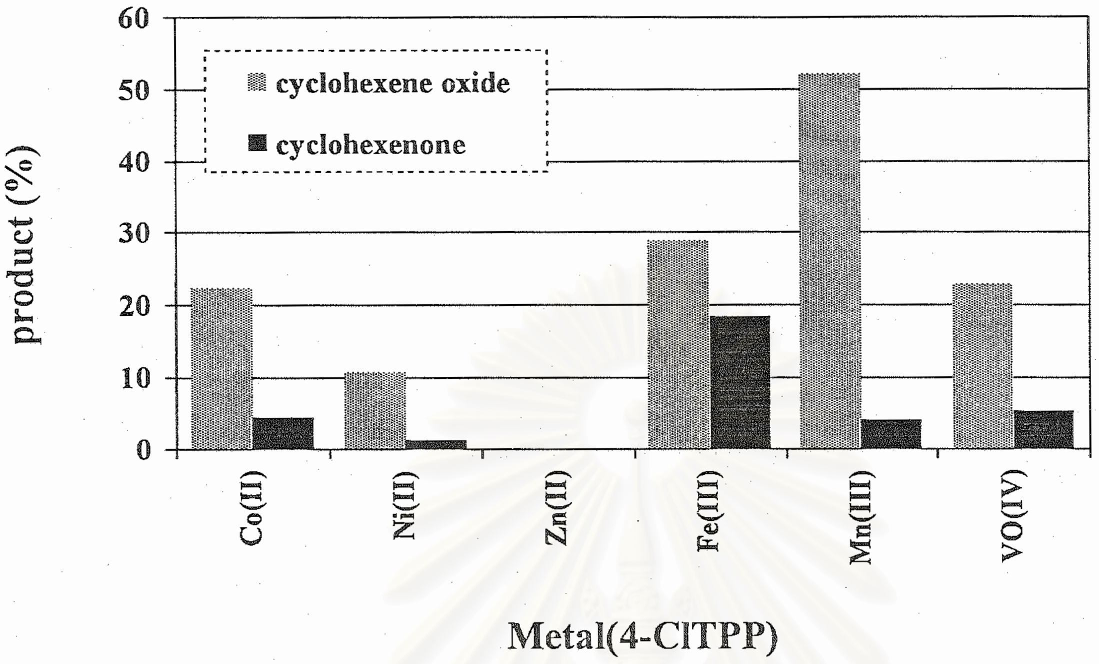


Fig 3.1 The epoxidation of cyclohexene catalyzed by metallo-tetrakis-4-chlorophenylporphyrins

From Table 3.1 and Fig 3.1, six transition metalloporphyrin complexes in the first row of the periodic table were screened for potentially catalytic epoxidation ability. It was found that the identity of the metal markedly affected the catalytic activity and selectivity of the catalyst. Among all catalyst complexes, the manganese complex provided the highest productivity of cyclohexene oxide and gave the best selectivity for the production of cyclohexene oxide over cyclohexenone. Therefore, manganese was the metal selected to form complexes with porphyrin ligands to further determine the effect of the porphyrin ligand on the epoxidation of cyclohexene.

3.3.1.2 Effect of porphyrin ligand

Manganese(III) porphyrin complexes containing a series of ligand at *meso*-positions of the porphyrin rings, both electron-donating and -withdrawing substituents on phenyl groups were examined to observe the effect of the porphyrin ligand on the epoxidation of cyclohexene. The outcomes of the utilization of the manganese(III) porphyrin complexe as catalyst are depicted in Table 3.2 and Fig 3.2.

Table 3.2 The epoxidation of cyclohexene catalyzed by manganese(III) porphyrins

Entry	Manganese(III) porphyrin	Product (%)		Selectivity Epoxide/Enone
		Cyclohexene oxide	Cyclohexenone	
1	4-BrTPP	9.63	1.91	5.04
2	3-ClTPP	8.49	2.17	3.91
3	4-ClTPP	52.13	4.14	12.59
4	4-CNTPP	12.49	3.72	3.36
5	3,4,5-OCH_3TPP	13.48	2.37	5.69
6	TPP	31.56	3.74	8.44
7	4-CH_3TPP	24.69	2.28	10.83
8	PTTPP	31.42	3.18	9.88

Reaction condition: Manganese(III) porphyrin 0.1 mmol, 2-ethylbutyraldehyde 10 mmol, cyclohexene 5 mmol, dichloromethane 30 mL, O_2, room temp and 24 hrs

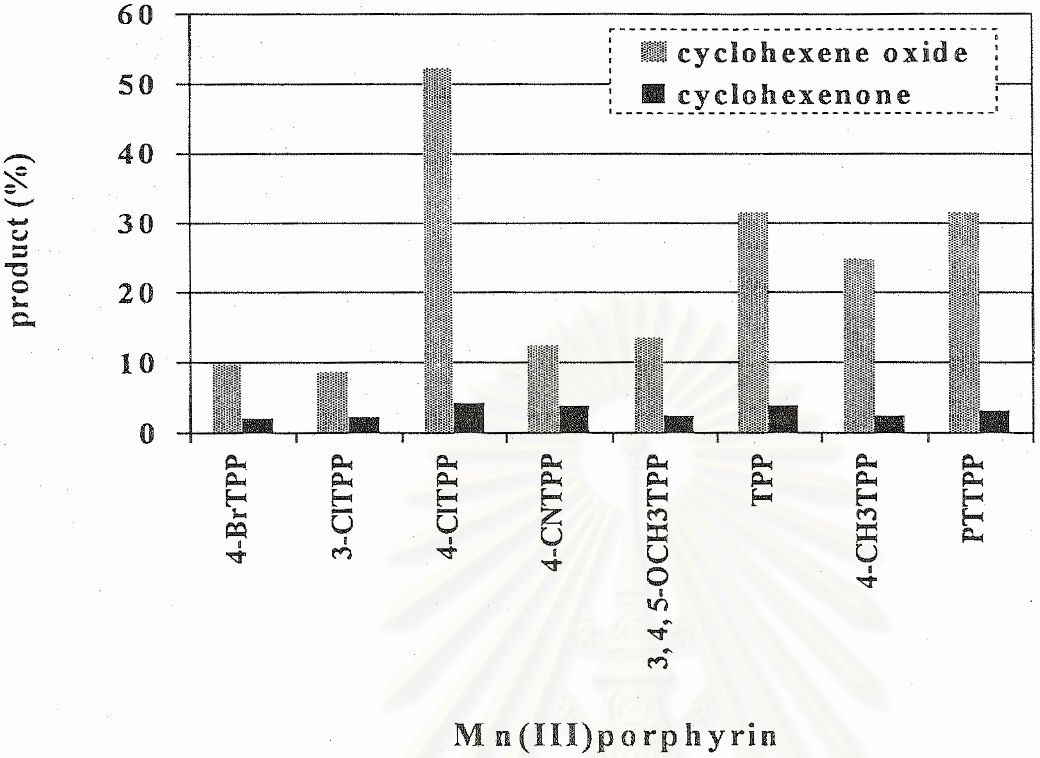


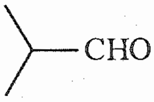
Fig 3.2 The epoxidation of cyclohexene catalyzed by manganese(III) porphyrins

The result in Table 3.2 clearly indicated that the porphyrin ligand played a leading role in the cyclohexene epoxidation. The steric and electronic effects of the phenyl ring substituents influenced the yield and selectivity of desired product, cyclohexene oxide. An highly steric-hindrance and electron-deficient porphyrin complex has the tendency to be a catalyst to achieve a high yield of oxygenated product by improving the lifetime of the catalyst or by retarding the catalyst's biomolecular self-destruction and promoting the rate of the oxygen transfer from the active intermediate to substrate.[74] In all catalysts tested, the manganese complex of electron-withdrawing substituents, *meso*-tetrakis-4-chlorophenylporphyrin, showed incomparable catalytic efficacy in both terms of reactivity and selectivity.

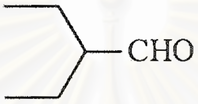
In conclusion, the productivity and selectivty to cyclohexene oxide was sensitive to the structure of the catalyst. Thus, the epoxidation of cyclohexene was critically dependent on the types of metal and porphyrin of metalloporphyrins. In this research, the usage of (*meso*-tetrakis-4-chlorophenylporphyrinato)manganese(III) chloride as catalyst for the cyclohexene epoxidation would be focused because of its high performance.

3.3.2 Effect of type of aldehyde

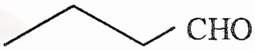
It is known that oxidant is a considerable key of epoxidation reaction. In this study aldehydes and oxygen were concentrated as oxidant, hence, the type of aldehyde was one of crucial parameters that needed to be explored to seek for the most proper aldehyde for the cyclohexene epoxidation. The findings of the application of several aldehydes are listed in Table 3.3 and Fig 3.3.



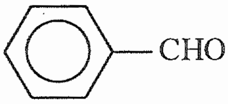
isobutyraldehyde



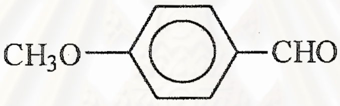
2-ethylbutyraldehyde



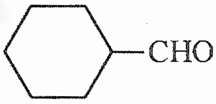
butyraldehyde



benzaldehyde



p-anisaldehyde



cyclohexane-carboxaldehyde

Table 3.3 The effects of aldehydes on the epoxidaton of cyclohexene

Entry	Aldehyde	Product (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	Epoxide/Enone
1	No	0	0	0
2	Anisaldehyde	0	0	0
3	Benzaldehyde	0	0	0
4	Butyraldehyde	0	0	0
5	Cyclohexane-carboxaldehyde	46.69	6.06	7.70
6	2-Ethylbutyraldehyde	52.13	4.14	12.59
7	Isobutyraldehyde	51.42	10.07	5.11

Reaction condition: Mn(III)4-ClTPP 0.1 mmol, aldehyde 10 mmol, cyclohexene 5 mmol, dichloromethane 30 mL, O_2, room temp and 24 hrs

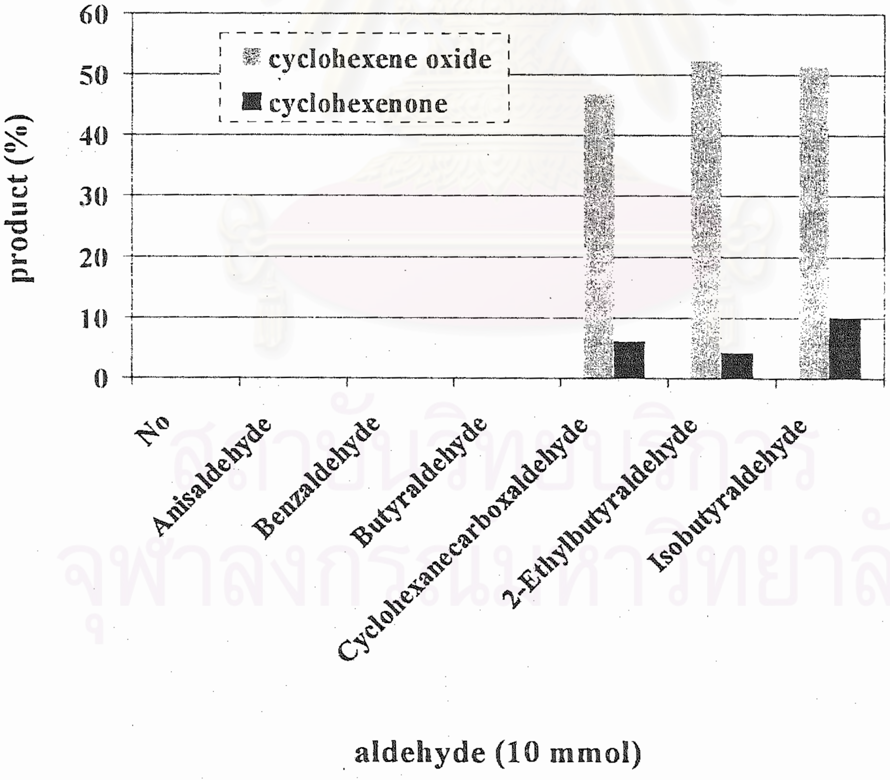


Fig 3.3 The effects of aldehydes on the epoxidation of cyclohexene

From Table 3.3 six aldehydes put to use in this part could be divided into three groups. First was an aldehyde moiety connecting a primary carbon such as butyraldehyde, another was an aldehyde functional group bearing with a secondary carbon like isobutyraldehyde, 2-ethylbutyraldehyde and cyclohexanecarboxaldehyde and the last was an aromatic aldehyde namely benzaldehyde and *p*-anisaldehyde. From the consequences displayed in Table 3.3, strongly pointed out that the aldehydes that connected to a secondary carbon exhibited impressive results. Especially 2-ethylbutyraldehyde spared good effects both of the yield and selectivity aspects of preferred product. On the other hand, the epoxidation reaction unoccurred when using either the aldehyde that connected to a primary carbon or aromatic aldehydes. Therefore, 2-ethylbutyraldehyde was considered as befitting aldehyde for the epoxidaton of cyclohexene.

3.3.3 Effect of solvent

In the investigations conducted above, dichloromethane was utilized as reaction medium because of its solubility in both metalloporphyrin catalysts and organic substrate, cyclohexene, exercised. The epoxidation reaction was further explored in a variety of other solvents. The upshots are summarized in Table 3.4 and Fig.3.4.

Table 3.4 The effects of solvents on the epoxidaton of cyclohexene

Entry	Solvent	Product (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	Epoxide/Enone
1	Acetonitrile	55.84	5.13	10.88
2	Benzene	36.38	4.53	8.03
3	Chloroform	36.87	4.99	7.39
4	1,2-Dichloroethane	46.39	7.64	6.07
5	Dichloromethane	52.13	4.14	12.59
6	Ethyl acetate	36.37	3.22	11.30
7	Methanol	23.17	2.94	7.88
8	Toluene	29.96	3.14	9.54

Reaction condition: Mn(III)4-ClTPP 0.1 mmol, 2-ethylbutyraldehyde 10 mmol, cyclohexene 5 mmol, solvent 30 mL, O_2, room temp and 24 hrs

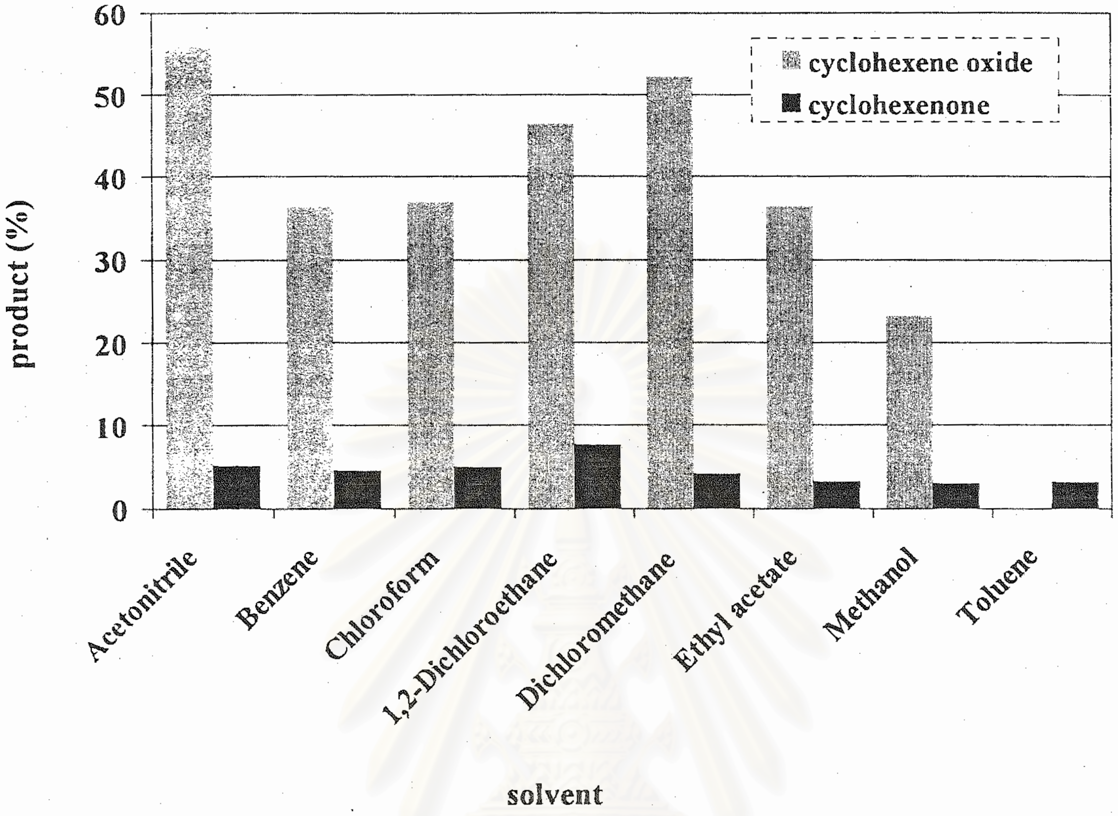


Fig 3.4 The effects of solvents on the epoxidaton of cyclohexene

From the results in Table 3.4, aliphatic solvents, in general, the yields of cyclohexene oxide were higher than both of aromatic solvents, benzene and toluene exceptionally metanol giving the lowest yield. Among aliphatic solvents, acetonitrile showed promising ability as solvent for the cyclohexene epoxidation due to it induced the highest yield and selectivity of cyclohexene oxide. Hence, the following examinations would be made use of acetonitrile as solvent.

3.3.4 Effect of the amount of 2-ethylbutyraldehyde

The end products of the effect of type of aldehyde in Table 3.3 intimated that 2-ethylbutyraldehyde was the best aldehyde for the cyclohexene epoxidation. Accordingly, the effect of the amount of 2-ethylbutyraldehyde was the next parameter that should be considered. The consequences are described in Table 3.5 and Fig 3.5.

Table 3.5 The effects of the amount of 2-ethylbutyraldehyde on the epoxidation of cyclohexene

Entry	2-Ethylbutyraldehyde (mmol)	Product (%)		Selectivity Epoxide/Enone
		Cyclohexene oxide	Cyclohexenone	
1	0	0	0	0
2	5	27.68	2.95	9.38
3	10	55.84	5.13	10.88
4	15	39.05	4.23	9.23
5	20	35.61	3.35	10.63

Reaction condition: Mn(III)4-ClTPP 0.1 mmol, 2-ethylbutyraldehyde 10 mmol, cyclohexene 5 mmol, acetonitrile 30 mL, O_2, room temp and 24 hrs

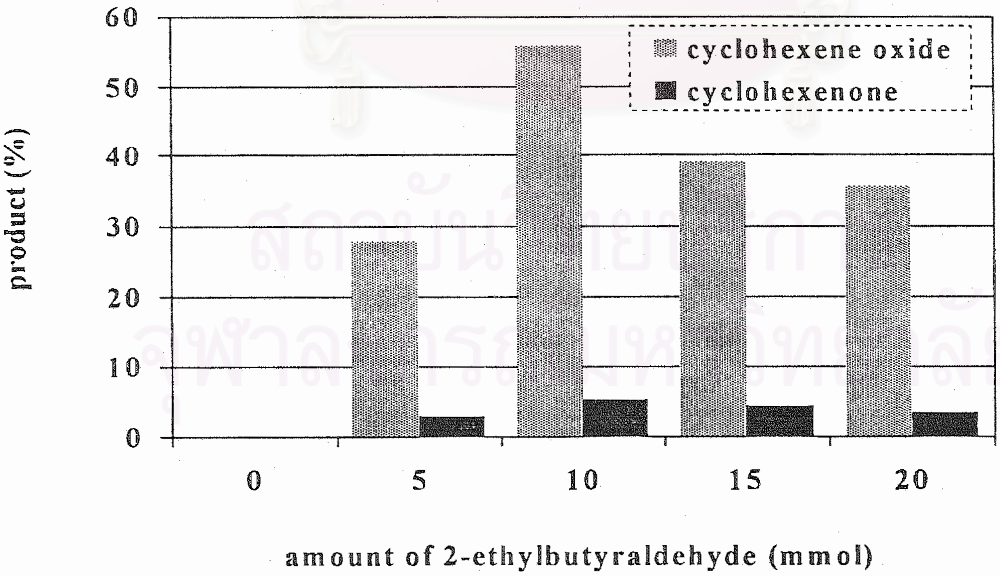


Fig 3.5 The effects of the amount of 2-ethylbutyraldehyde on the epoxidation of cyclohexene

In the blank experiment (entry 1), it was apparently revealed that the epoxidation did not occur in the absence of 2-ethylbutyraldehyde. In the presence of 2-ethylbutyraldehyde, cyclohexene oxide was readily produced but only the low yield in entry 2. Cyclohexene oxide enhanced about 2 times in the addition of the aldehyde from 5 to 10 mmol. However, the yields of cyclohexene oxide reduced indicated that it did not improve the yield of cyclohexene oxide when using 2-ethylbutyraldehyde more than 10 mmol. For this reason, 10 mmol of 2-ethylbutyraldehyde was the most suitable amount for the epoxidation of cyclohexene under this particular condition.

3.3.5 Effect of the amount of cyclohexene

Owing to only about 60 % of total product observed (Table 3.5, entry 3) and the GC chromatogram of the residue of the reaction operating at 5 mmol of the substrate, cyclohexene, demonstrated that cyclohexene still remained after the epoxidation. It was pointed out that cyclohexene utilized was extravagant and should be optimized by diminishing in quantity. The sequels of this are expressed in Table 3.6 and Fig 3.6.

Table 3.6 The effects of the amount of cyclohexene on the epoxidation reaction

Entry	Cyclohexene (mmol)	Product (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	Epoxide/Enone
1	2	27.26	1.77	15.40
2	3	51.38	3.92	13.11
3	4	83.09	12.57	6.61
4	5	63.40	5.64	11.24

Reaction condition: Mn(III)4-ClTPP 0.1 mmol , 2-ethylbutyraldehyde 10 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

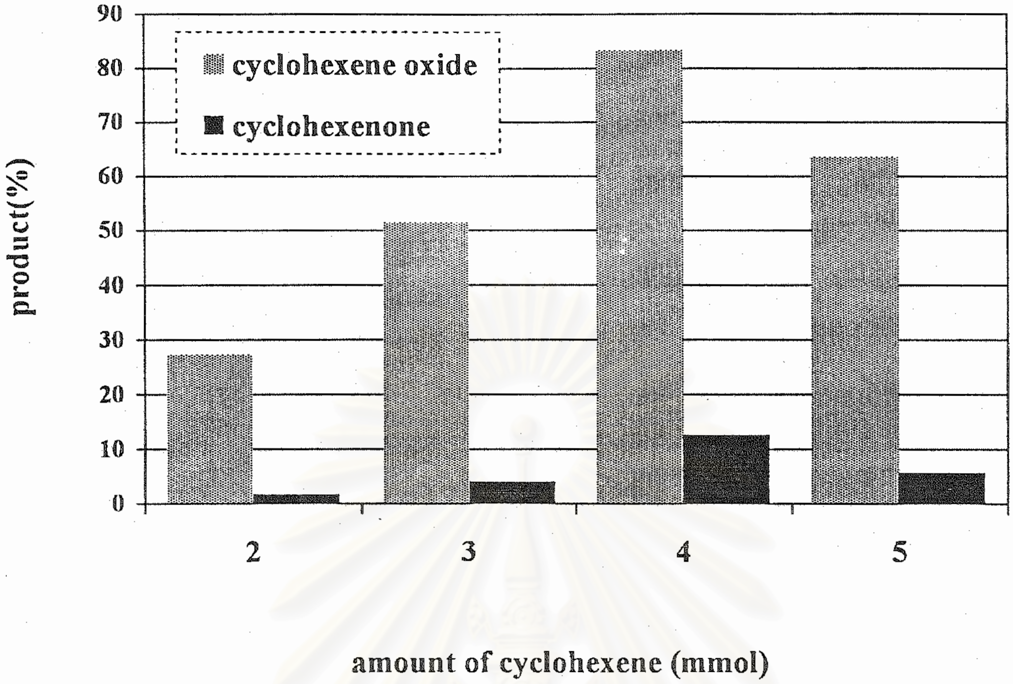


Fig 3.6 The effects of the amount of cyclohexene on the epoxidation reaction

Clearly, in entry 3, the yield of cyclohexene oxide rocketed up from about 63 to 83 % as the result of the decrease of 20 % to the amount of cyclohexene handled. Conversely, the yields of cyclohexene oxide were dropped dramatically as the decreasing of cyclohexene in entries 1 and 2. Therefore, the amount of cyclohexene well chosen was 4 mmol.

3.3.6 Effect of the amount of catalyst

The last inquiring parameter followed up in this research was the effect of the amount of the catalyst, (*meso*-tetrakis-4-chlorophenylporphyrinato)manganese(III) chloride, employed. It was beneficial to study the relationship between the catalyst amount consumed and its catalytic activity and selectivity and to estimate the optimum point of amount of the catalyst which the catalyst was exhausted at least but afforded the most profitable as possible in the facets of the yield and selectivity of pursued product. The amount of the catalyst was scrutinized in the range of 0.025 to 0.200 mmol. The upshots of the cyclohexene epoxidation are shown in Table 3.7 and Fig 3.7.

Table 3.7 The effects of the amount of (*meso*-tetrakis-4-chlorophenylporphyrinato) manganese(III) chloride on the epoxidation of cyclohexene

Entry	Mn(III)4-ClTPP (mmol)	Product (%)		Selectivity (1)/(2)	(1)+(2)
		(1)	(2)		
1	0.025	65.31	8.39	7.78	73.70
2	0.050	84.78	13.08	6.48	97.86
3	0.100	83.09	12.57	6.61	95.66
4	0.150	83.45	12.72	6.56	96.17
5	0.200	83.12	13.02	6.38	96.14

Reaction condition: Mn(III)4-ClTPP, 2-ethylbutyraldehyde 10 mmol, cyclohexene 4 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

(1) = cyclohexene oxide, (2) = cyclohexenone

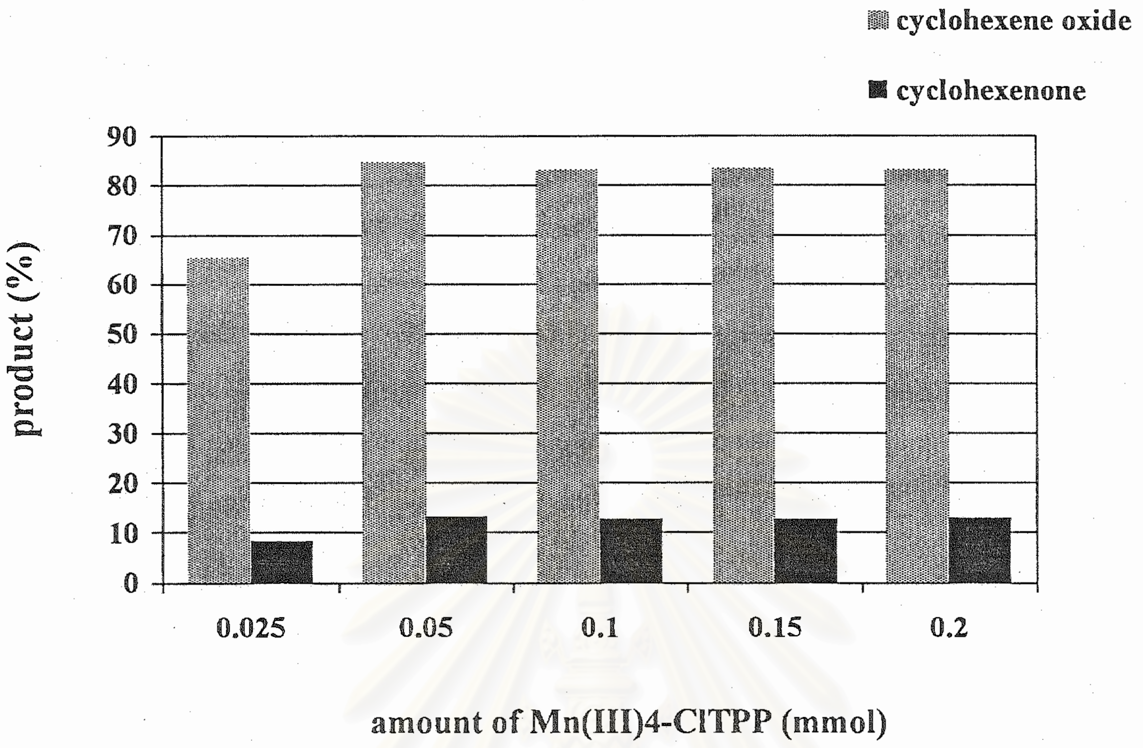


Fig 3.7 The effects of the amount of (*meso*-tetrakis-4-chlorophenylporphyrinato) manganese(III) chloride on the epoxidation of cyclohexene

From the alteration of the amount of the catalyst, cyclohexene oxide was obtained in moderate yield at the lowest concentration (entry 1). Increasing the amount of the catalyst to 0.05 mmol (entry 2) the product selectivity was gained slightly lower than the former, but in the term of catalytic activity, cyclohexene oxide was attained in greatly higher yield. Moreover, the total yield of the reaction was close to 100, which pointed out that the reaction could proceed almost completely. Above 0.05 mmol of the catalyst, the cyclohexene yield scarcely fell and leveled off at about 83 % while the selectivity of the cyclohexene oxide and the total yield of the reaction were not divergent. As consequence, the amount of the catalyst used could be reduced to 0.05 mmol whereas the reaction system still furnished the best result.

3.4 Stability study of cyclohexene oxide

Because cyclohexene oxide is the major product in demand from epoxidation reaction, stability of cyclohexene oxide transpired in the reaction condition operated is very meaningful. In most case of the explorations inquired before, the cyclohexene epoxidations were reacted under the condition using (*meso*-tetrakis-4-chlorophenylporphyrinato)manganese(III) chloride as catalyst, 2-ethylbutyraldehyde and oxygen as oxidant and acetonitrile as solvent at room temperature. Therefore, the stability of cyclohexene oxide was tested under this condition. The reaction performed without the catalyst under the same condition was compared to inspect whether any further reactions of cyclohexene oxide occurred. The outcomes are listed in Table 3.8.

Table 3.8 Stability of cyclohexene oxide

Entry	Mn(III)4-ClTPP (mmol)	Recovered cyclohexene oxide (%)
1	No	95.15
2	0.1	90.36

Reaction condition: 2-ethylbutyraldehyde 10 mmol, cyclohexene oxide 5 mmol, acetonitrile 30 mL, O_2, room temp and 24 hrs

In case of having the catalyst in entry 2, a little cyclohexene oxide disappeared disclosed that the further reaction that transformed cyclohexene oxide to others had no significance. Therefore, cyclohexene oxide had high stability in this system. Indeed, the difference of cyclohexene oxide left after both reactions exposed that the catalyst generated active species greatly specific to cyclohexene than cyclohexene oxide. In other word, the catalytic system utilized in this research was good for the epoxidation of cyclohexene.

3.5 Comparative kinetic study of the epoxidation of cyclohexene catalyzed by various metalloporphyrins

Numerous metalloporphyrins can catalyze epoxidation of cyclohexene to proceed at room temperature. Nevertheless, the rates of these reactions are generally disparate and kinetic studies of these catalysts are requisite to demonstrate required times of each system to complete the reactions. The catalytic system that consumes less time and provides high desired productivity would be primarily needed. Five metalloporphyrin complexes, Mn(III)4-ClTPP, Mn(III)TPP, Mn(III)PTTPP, Co(III)4-ClTPP and Fe(III)4-ClTPP were chosen as the representatives for the kinetic study of metalloporphyrins on the rate of the cyclohexene epoxidation. The kinetic results are shown in Table 3.9 and Fig 3.8.

Table 3.9 Kinetic study of the epoxidation of cyclohexene catalyzed by various metalloporphyrins

Time (hrs)	Cyclohexene oxide (%)				
	Mn(III)4-ClTPP	Mn(III)TPP	Mn(III)PTTPP	Co(II)4-ClTPP	Fe(III)4-ClTPP
1	27.03	7.25	5.68	22.27	32.55
2	48.18	12.08	15.58	43.52	53.09
4	62.87	27.96	28.96	52.41	66.63
8	64.78	25.01	29.05	50.01	70.90
12	63.81	23.15	26.37	44.96	66.02

Reaction condition: Metalloporphyrin 0.05 mmol, 2-ethylbutyraldehyde 5 mmol, cyclohexene 2.5 mmol, acetonitrile 15 mL, O_2 and room temp

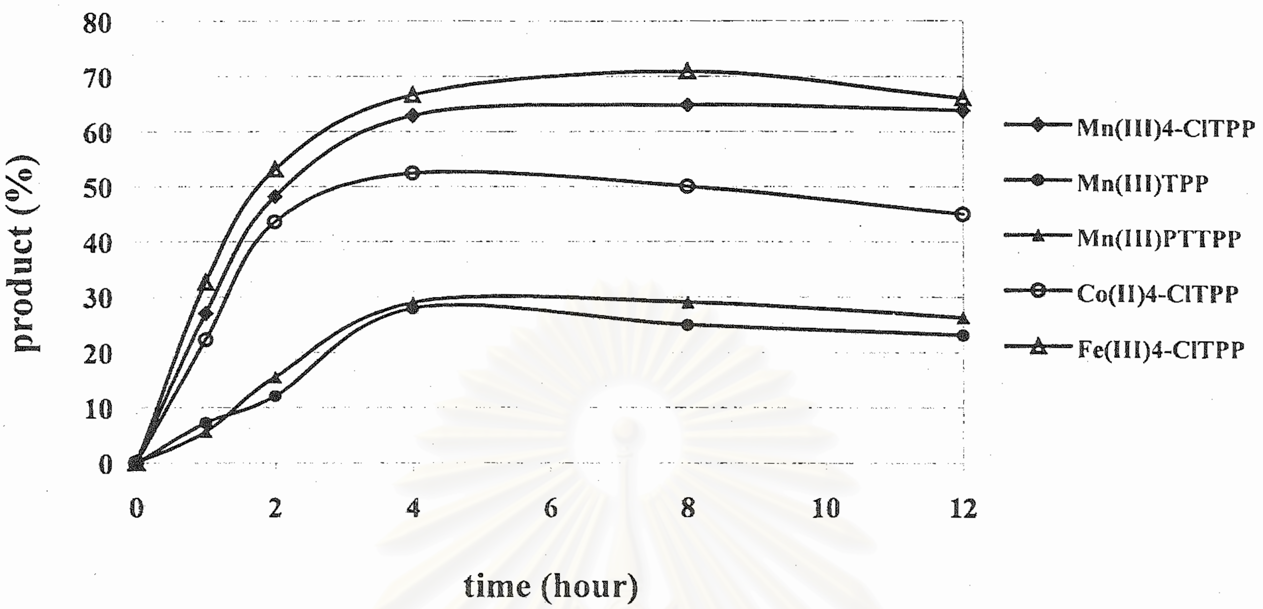


Fig 3.8 Kinetic study on the cyclohexene epoxidation catalyzed by various metalloporphyrin complexes

Half-life of the reaction is a significant factor to reflect the kinetic epoxidation rate of the system. The reaction with lesser half-life would proceed faster and therefore would be more applicable. The half-life of the catalysts employed in the cyclohexene epoxidation reactions was calculated and presented in Table 3.10.

However, the elucidation of the reaction rate by considering the half-life of the reaction only was tactless in some cases, especially when the product quantity obtained at the optimum time in each system was dramatically diverse. Thus, there should be discussed concurrently with another approach such as kinetic curve analysis.

Table 3.10 Half-life of various catalysts studied in the cyclohexene epoxidation

Catalyst	Hale-life (min)
Mn(III)4-ClTPP	73
Mn(III)TPP	135
Mn(III)PTTPP	114
Co(II)4-ClTPP	76
Fe(III)4-ClTPP	63

As Fig 3.8, all kinetic curves had the resemble trend that climbed steadily to reach a peak and then started to come down except in case of Mn(III)4-ClTPP which was rather constant after reaching the peak. The reactions could achieve within 4 hrs.

The kinetic study result in this work was analyzed according to the epoxidation catalyst, which could be divided into two groups. The first was manganese complexes of different porphyrins, Mn(III)4-ClTPP, Mn(III)TPP, and Mn(III)PTTPP which would be focused to determine the effect of porphyrin ligand around the metal ion on the rate of the cyclohexene epoxidation. It was found that the rate of the catalytic epoxidation by Mn(III)4-ClTPP, whose porphyrin substituents were electron-withdrawing, was the highest rate. The order of the reactivity of the catalyst illustrated with the reaction rate or half-life value was Mn(III)4-ClTPP > Mn(III)PTTPP > Mn(III)TPP. The second was three metal complexes of *meso*-tetrakis-4-chlorophenylporphyrin, Mn(III)4-ClTPP, Fe(III)4-ClTPP and Co(II)4-ClTPP. Like the first group, this series of the experiment revealed the importance of the metal of the catalyst complex. The appropriate metal could facilitate the epoxidation reaction to take place at satisfying rate. The order of the rate of the epoxidation reaction catalyzed by Fe(III)4-ClTPP > Mn(III)4-ClTPP > Co(II)4-ClTPP.

3.6 Comparative reactivity study of Co(II)-, Fe-(III) and Mn(III)4-ClTPP on the epoxidation of cyclohexene

From the comparative kinetic study of metalloporphyrin catalysts explored above, the results displayed the fascinating catalytic ability of Fe(III)4-ClTPP to catalyze the epoxidation of cyclohexene. The half-life presented that the rate of the reaction catalyzed by Fe(III)4-ClTPP was slightly faster than that of Mn(III)4-ClTPP. Consequently, Fe(III)4-ClTPP would be tested for their efficiency as catalyst in the optimum condition for the epoxidation of cyclohexene using Mn(III)4-ClTPP. Other interesting metalloporphyrin complex like Co(II)4-ClTPP was also examined. The findings of the utilization of these catalysts are described and compared with Mn(III)4-ClTPP in Table 3.11 and Fig 3.9.

Table 3.11 The epoxidation of cyclohexene catalyzed by Co(II)-, Fe(III)- and Mn(III)4-ClTPP.

Entry	Metal(4-ClTPP)	Product (%)		Selectivity
		Cyclohexene oxide	Cyclohexenone	Epoxide/Enone
1	Co(II)	49.00	9.14	5.36
2	Fe(III)	60.05	9.41	6.38
3	Mn(III)	84.78	13.08	6.48

Reaction condition: Metal(4-ClTPP) 0.05 mmol, 2-ethylbutyraldehyde 10 mmol, cyclohexene 4 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

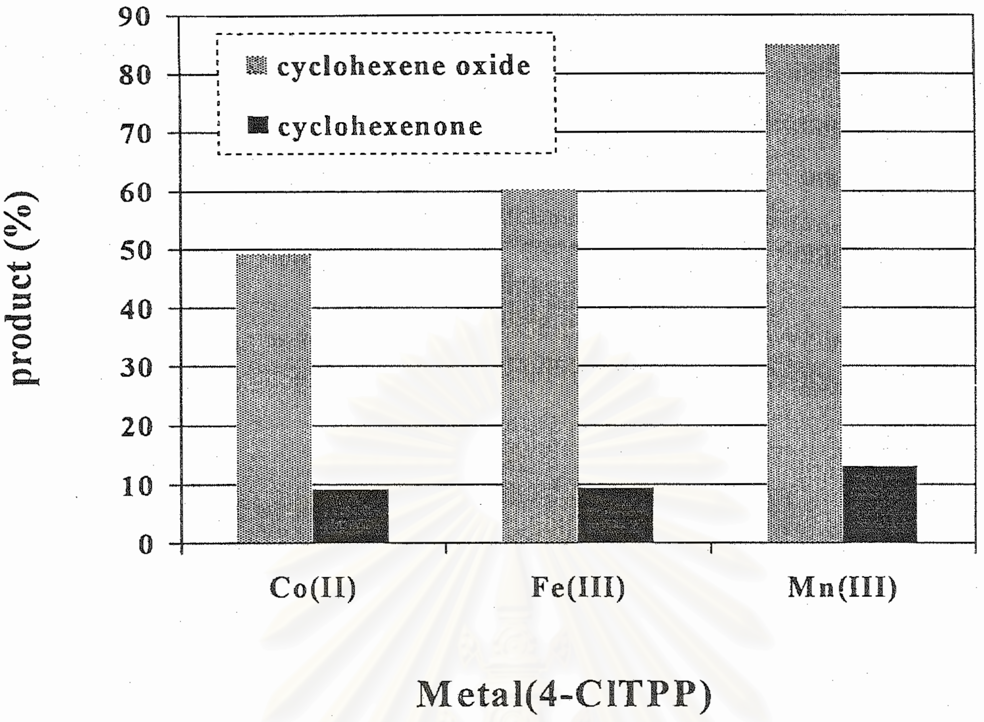


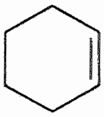
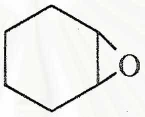
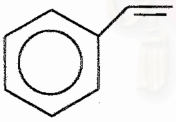
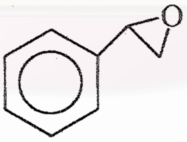
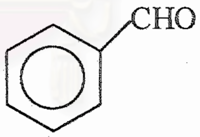
Fig 3.9 The epoxidation of cyclohexene catalyzed by Co(II)4-ClTPP, Fe(III)4-ClTPP and Mn(III)4-ClTPP.

Apparently, Mn(III)4-ClTPP turned out to be the best potential catalyst for the epoxidation of cyclohexene under the particular condition. Mn(III)4-ClTPP showed district competence to catalyze the epoxidation in highest reactivity giving good yield whereas Co(II)4-ClTPP and Fe(III)4-ClTPP gave cyclohexene oxide as product just in moderate yield. This upshot obviously indicated that the metal center of the metal complex had great influence on the catalytic activity of the catalyst.

3.7 Application of the developed epoxidation reaction

The optimum condition for the epoxidation of the endocyclic alkene namely cyclohexene, picked out as first chemical model, could be summarized as follows: 4 mmol of cyclohexene as substrate, 30 mL of acetonitrile as solvent, 0.05 mmol of Mn(III) 4-ClTPP as catalyst, oxygen and 10 mmol of 2-ethylbutyraldehyde as oxidant in reaction time 4 hrs at room temperature. Under this condition, cyclohexene was smoothly converted to cyclohexene oxide in high yield with a trace of the allylic oxidation product occurred. In this section, the knowledge of this would be applied to enlarge epoxidation reactions of other types of alkene. The epoxidations of 1-dodecene and styrene, which were the representatives of aliphatic and aromatic terminal alkenes, were carried out under the specific condition. The end products are represented in Table 3.12.

Table 3.12 The Mn(III)4-ClTPP-catalyzed epoxidation of various alkenes

Entry	Substrate	Product (%)	Recovered substrate (%)
1		 84.78  13.08	2.14
2		 14.44	76.55
3		 56.29  7.90	16.05

Reaction condition: Mn(III)4-ClTPP 0.05 mmol, 2-ethylbutyraldehyde 10 mmol, substrate 4 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

For the epoxidation of 1-dodecene, the reaction gave low yield of the desired product, 1-dodecene oxide. It was not surprising because the epoxide of terminal alkenes, generally, was difficult to prepare. A lot of the recovered substrate detected pointed out that this substrate was unreactive.

In the case of the epoxidation of styrene, the substrate could be transformed to styrene oxide in moderate yield with a little concurrence of benzaldehyde as minor product from cleaving of the terminal double bond. Compared with the epoxidation of 1-dodecene, the corresponding epoxide from the epoxidation of styrene was obtained much higher indicating the terminal double bond conjugated to aromatic ring was easier to be epoxidized to the epoxide or had more preference to occur epoxidation reaction than the aliphatic terminal double bond. It was probably owing to the aromatic ring could act as good electron-donating source.

3.7.1 The epoxidation of 1-dodecene

3.7.1.1 Effect of amount of substrate on the epoxidation of 1-dodecene

As Table 3.12, the result of the epoxidation obviously disclosed that the optimum condition of the epoxidation of cyclohexene was inapt for the epoxidation of 1-dodecene. To improve its potential to better production, the reaction system should be balanced some parameters. The first one giving cause for concern was the amount of the substrate, 1-dodecene, because high recovered substrate was observed. The effects of the amount of 1-dodecene are illustrated in Table 3.13 and Fig 3.10.

Table 3.13 The effects of the amount of 1-dodecene on the epoxidation of 1-dodecene

Entry	1-Dodecene (mmol)	Yield (%)	
		1-Dodecene oxide	Recovered 1-dodecene
1	1	62.76	24.82
2	2	47.75	39.71
3	4	14.44	76.55

Reaction condition: Mn(III)4-ClTPP 0.05 mmol , 2-ethylbutyraldehyde 10 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

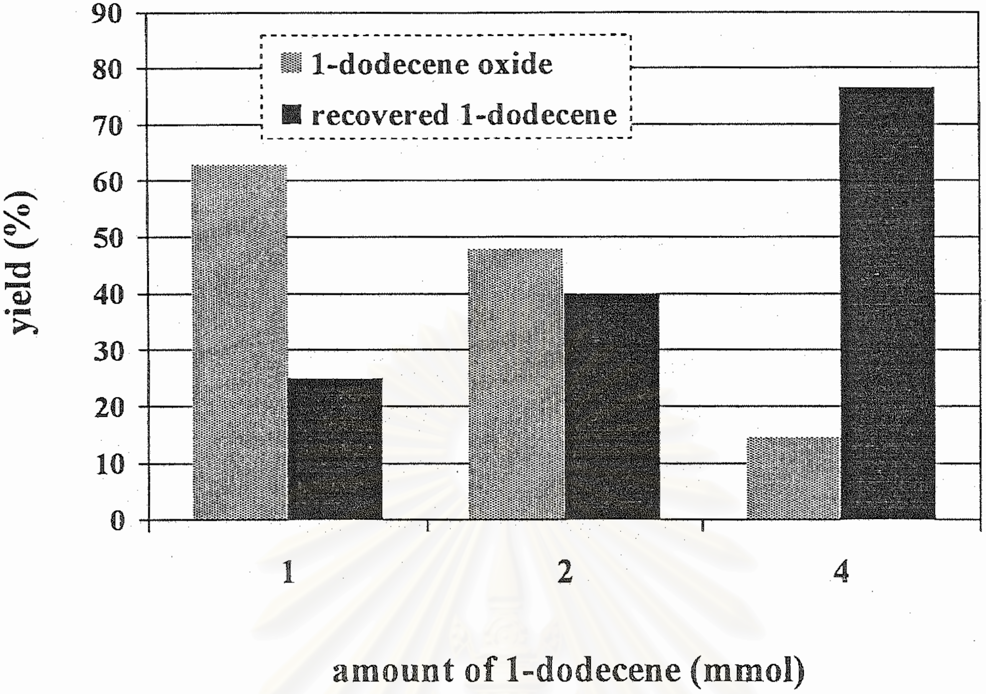


Fig 3.10 The effects of the amount of 1-dodecene on the epoxidation reaction

In the diminution of the amount of 1-dodecene ranged from 4 to 1 mmol, the yield of 1-dodecene oxide required rose from about 14 to 62 %. Thus, it was clearly seen that decreasing the substrate handled caused the substrate conversion and desired product rapidly increased. From these observations, 1 mmol of 1-dodecene was fit to give dodecene oxide in the highest yield.

3.7.1.2 Effect of reaction time on the epoxidation of 1-dodecene

It is known that the aliphatic terminal alkene like 1-dodecene is hard to be epoxidized and the epoxidation rate is slow. As proceeding, all epoxidations of 1-dodecene were carried out at 4 hrs and the maximum yield was received just about 62 %. Theoretically, alkenes could be fully epoxidized at one point if the epoxidizing time is prolonged enough. Accordingly, it would be well worthwhile to elongate the epoxidation time to complete the reaction. The sequels of the effect of the reaction time on the 1-dodecene epoxidation are exhibited in Table 3.14 and Fig 3.11.

Table 3.14 The effects of the reaction time on the 1-dodecene epoxidation

Entry	Time (hrs)	1-dodecene oxide (%)
1	4	62.76
2	6	74.70
3	8	81.17
4	10	71.21
5	12	75.11

Reaction condition: Mn(III)4-ClTPP 0.05 mmol, 1-dodecene 1 mmol, 2-ethylbutyraldehyde 10 mmol, acetonitrile 30 mL, O_2 and room temp

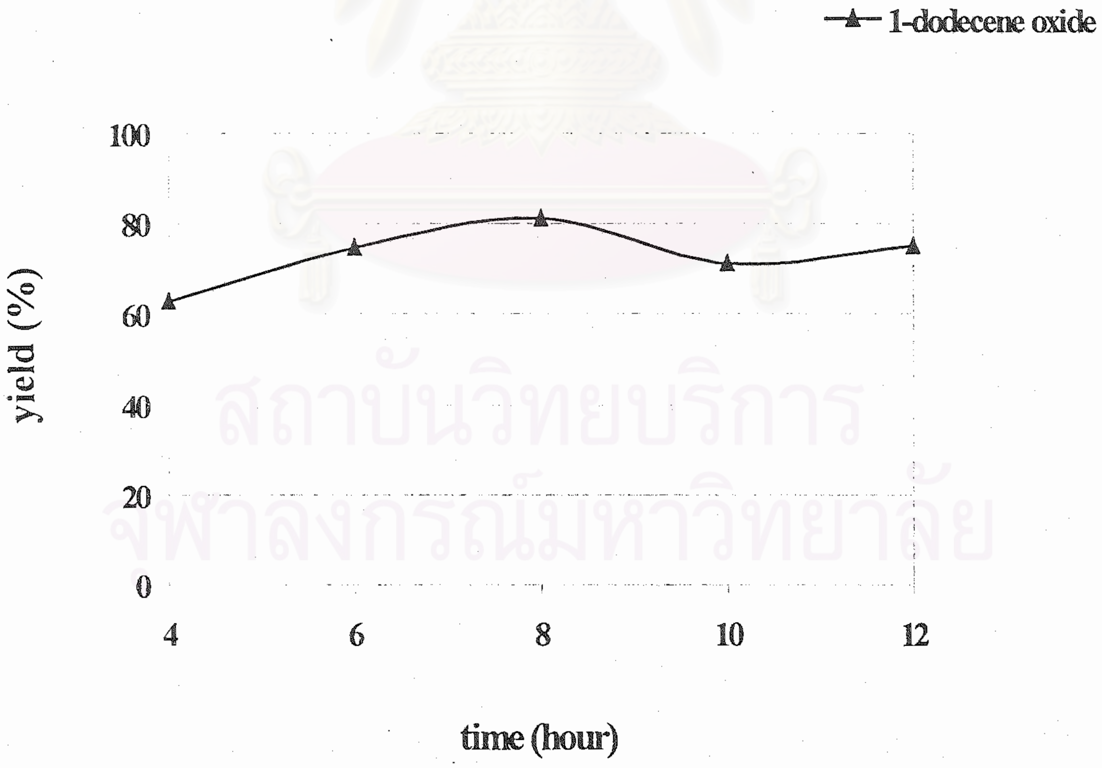


Fig 3.11 The effects of reaction time on the 1-dodecene epoxidation

Fig 3.11 depicted the productivity of desired product, 1-dodecene oxide gained at the varied reaction time from 4 to 12 hrs. The resulting yield of 1-dodecene oxide was plotted versus the reaction time. The outcome clarified that the 1-dodecene epoxidation required the time more than 4 hrs to complete the reaction. The increase in reaction time improved on 1-dodecene oxide productivity in the range of 4-8 hrs. 8 Hours were taken as the most favorable reaction time at which the maximum epoxidation was reached. After 8 hrs, there was a start to decline in the productivity of 1-dodecene oxide.

To sum up from this study, the finest catalytic system of the 1-dodecene epoxidation was consisted of 1 mmol of 1-dodecene as substrate, 30 mL of acetonitrile as solvent, 0.05 mmol of Mn(III)4-ClTPP as catalyst, oxygen and 2-ethylbutyraldehyde as oxidant in reaction time 8 hrs at room temperature. The 1-dodecene oxide yield was risen to 81%.

3.7.2 The epoxidation of styrene

3.7.2.1 Effect of the amount of substrate on the epoxidation of styrene

Like the epoxidation of 1-dodecene, the amount of the substrate, styrene, was the crucial parameter, which was taken into further consideration to be evaluated. The variation of the amount of the substrate was explored in the range of 1.5 to 4.0 mmol. The results are exhibited in Table 3.15 and Fig 3.12.

Table 3.15 The effects of the amount of styrene on the epoxidation reaction

Entry	Styrene (mmol)	Product (%)		Selectivity
		Styrene oxide	Benzaldehyde	Epoxide/Aldehyde
1	1.5	82.85	9.75	8.50
2	2.5	71.73	9.04	7.93
3	3.5	62.98	8.63	7.30
4	4.0	56.29	7.99	7.05

Reaction condition: Mn(III)4-ClTPP 0.05 mmol , 2-ethylbutyraldehyde 10 mmol, acetonitrile 30 mL, O_2, room temp and 4 hrs

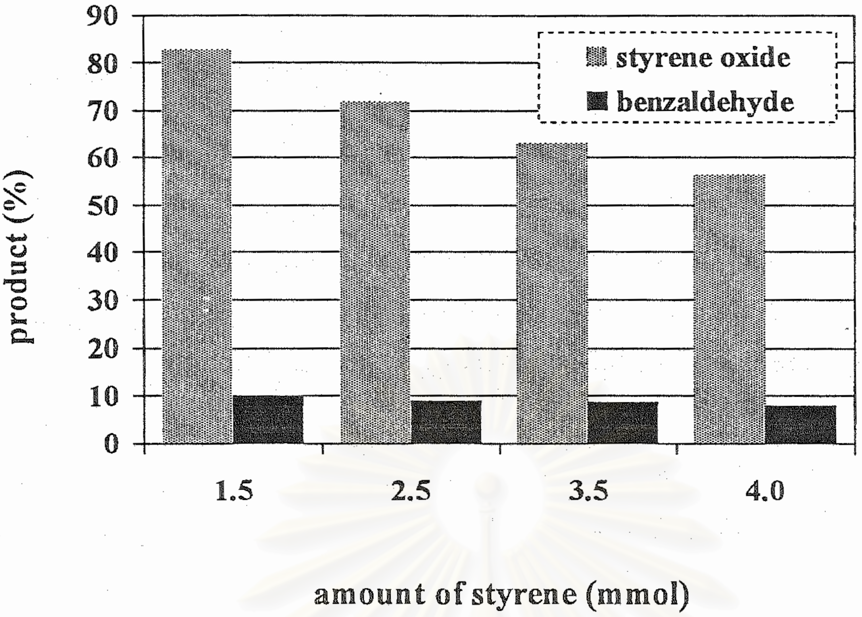


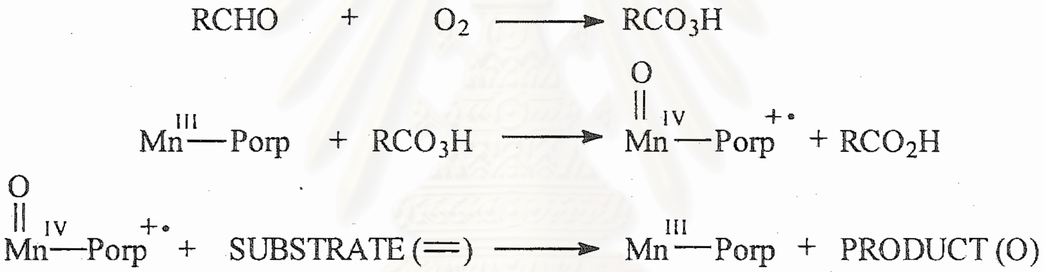
Fig 3.12 The effects of the amount of styrene on the epoxidation reaction

In Fig 3.12, both of the craved product, styrene oxide and styrene conversion steadily increased with the continuous decrease of the styrene substrate. Considering about the reaction selectivity, the consequence also uncovered the conguous trend. Among the amount of the substrate tested, 1.5 mmol of styrene was the most suitable giving the highest yield of styrene oxide and the greatest selectivity of styrene oxide to benzaldehyde.

From this investigation, the optimum condition for the epoxidation of styrene was obtained and could be concluded as follows: 1.5 mmol of styrene as substrate, 30 mL of acetonitrile as solvent, 0.05 mmol of Mn(III)4-ClTPP as catalyst, oxygen and 2-ethylbutyraldehyde as oxidant in reaction time 4 hrs at room temperature. Under this condition, styrene was easily transmuted to styrene oxide in providing intriguing results in all aspects of productivity and selectivity.

3.8 Proposed mechanism for the Mn(III)4-ClTPP-catalyzed epoxidation of alkenes

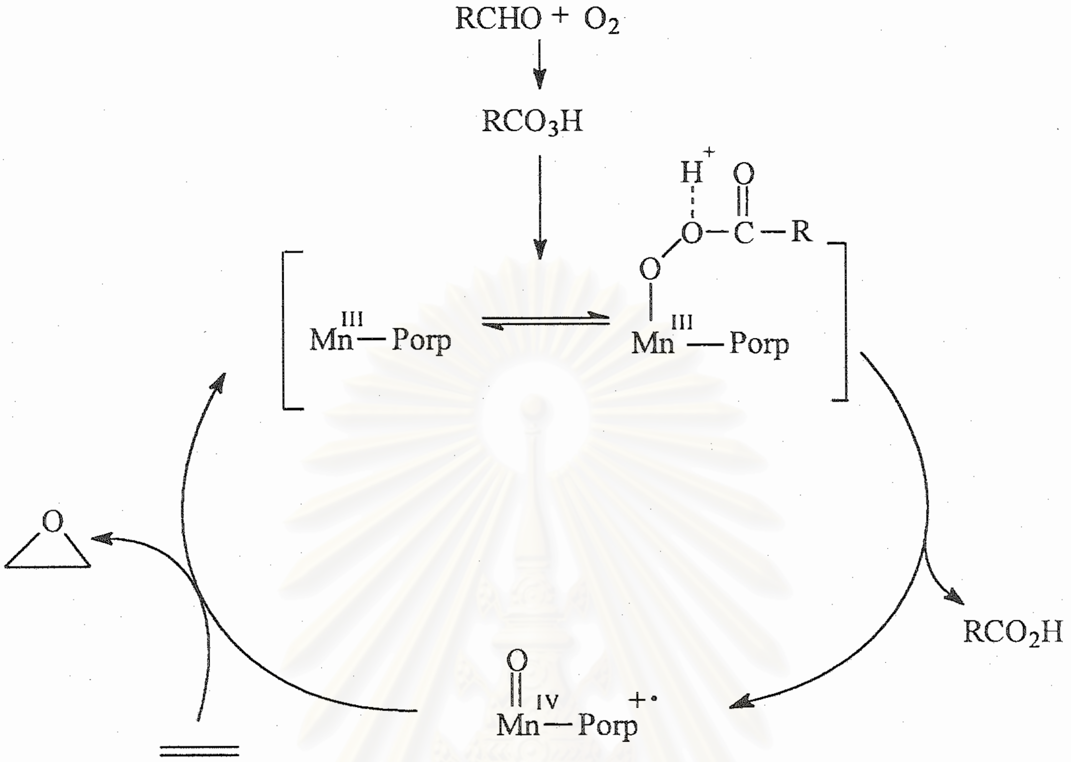
As biomimic models for the metalloenzymes, the reactions of metalloporphyrin complexes with various oxidants have been extensively studied with the intention of elucidating the mechanism of the oxygen activation and oxygen atom transfer reactions. Because the high valent metal(IV) oxoporphyrin cation radical intermediates play a key role in the alkene epoxidation reactions by metalloporphyrins, the machanism of the Mn (III)4-ClTPP-catalyzed epoxidation of alkenes using molecular oxygen and aldehyde as oxidant in this research was proposed on the basis of the intermediate species. The epoxidation was therefore submitted to occur *via* the free radical pathway.[60,72] The proposed mechanism is shown in Scheme 3.1



$$\mathrm{RCHO} + \mathrm{O_2} \longrightarrow \mathrm{RCO_3H}$$

$$\overset{\mathrm{III}}{\mathrm{Mn}}\text{—Porp} + \mathrm{RCO_3H} \longrightarrow \overset{\overset{\mathrm{O}}{\|}}{\mathrm{Mn}}{}^{\mathrm{IV}}\text{—Porp}^{+\bullet} + \mathrm{RCO_2H}$$

$$\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Mn}}{}^{\mathrm{IV}}\text{—Porp}^{+\bullet} + \text{SUBSTRATE}\,(=) \longrightarrow \overset{\mathrm{III}}{\mathrm{Mn}}\text{—Porp} + \text{PRODUCT}\,(\mathrm{O})$$



Scheme 3.1 The proposed mechanism for the Mn(III)4-ClTPP-catalyzed epoxidation of alkenes

As this mechanism, an aldehyde and oxygen react, generating a peroxy acid. The catalytic cycle started with the reaction of the manganese(III) porphyrin complex with the peroxy acid which was in the equilibrium with the manganese(III) peroxy complex obtained. Then, the O-O bond of the manganese(III) peroxy complex was cleaved heterolytically resulting in the formation of the high valent manganese(IV) oxoporphyrin cation radical intermediate as reactive species in the epoxidation reaction and the corresponding acid as by product. The reactive species was believed to transfer the oxygen directly to the alkene and the manganese(III) complex renewed to the catalytic cycle.

CHAPTER IV

CONCLUSION AND SUGGESTION

4.1 Conclusion

Catalytic epoxidation chemistry was of considerable area of this research. Practical efficient methodology toward selective alkene epoxidation remains an important goal. The study was carried on the homogeneous metalloporphyrin catalyst system with a combination of an aldehyde and oxygen oxidant at room temperature. The metalloporphyrin catalyst was found to play a key role in the epoxidation of cyclohexene. Effects of the metal center and porphyrin ligand of the catalyst on productivity and selectivity of desired product were observed. The epoxidation was also as a function of type and amount of aldehyde, type of solvent and amount of substrate used. Cyclohexene 4 mmol as substrate, Mn(III)4-ClTPP 0.05 mmol as catalyst, acetonitrile 30 mL as solvent, 2-ethylbutyraldehyde 10 mmol and oxygen as oxidant in the reaction period 4 hrs was discovered to be the optimum condition. The product stability study showed that the active species of the reaction was unspecific for cyclohexene oxide led to high stability of cyclohexene oxide in this system. Under this particular operation, the maximum cyclohexene oxide yield, ca. 85% was reached.

Epoxidation study was also widen to other types of alkene. Application based upon the developed epoxidation reaction to epoxidations of 1-dodecene and styrene, aliphatic and aromatic terminal alkenes, was achieved. 1-Dodecene and styrene were smoothly converted to their corresponding epoxides in high yields, ca 81 % and 83 % respectively.

As for the comparative kinetic study, some interesting clues were attained. The outcome implied that the rate of the cyclohexene epoxidation catalyzed by electron-defficient porphyrin complex was faster than that of electron-rich porphyrin complex. Among all manganese complexes, Mn(III)4-ClTPP could catalyze the epoxidation to proceed at the highest rate. The half-life of the epoxidation was 73 minutes and the reaction could be finished within 4 hrs. The mechanism of the alkene epoxidation was believed to occur *via* free radical pathway. High valent manganese(IV) oxoporphyrin cation radical intermediate was accepted as active oxidizing agent to epoxidize alkenes.

To our best knowledge, the utilization of the Mn(III)4-ClTPP-2-ethylbutyraldehyde-oxygen catalytic system has no report in chemical literatures for the alkene epoxidation. From the result of this research, it was worthwhile to conclude that the catalytic system was useful for all epoxidations of cyclohexene, 1-dodecene and styrene. Undoubtedly, it can be a new alternative way to the epoxide production.

4.2 Suggestion for the further work

Interestingly, intensive regioselectivity and stereoselectivity studies of this catalytic system will be investigated by asymmetric epoxidations of various alkenes such as 1-methylcyclohexene, 1-ethylenecyclohexene, 3-*tert*-butylcyclohexene and α-methylstyrene. In addition, the oxidation of other hydrocarbons including alkane, alcohol and amine would be another challenging topic to continually examine.

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