

Chapter I

Introduction



In Thailand, hazardous waste is becoming a major problem, especially, used solvents, toxic chemicals and metal pollutants discharged from factories. In the manufacturing of polystyrene from the polymerization of distilled styrene monomer, large amount of styrene waste is usually left from distillation of styrene monomers. Currently, this waste generates potential problem on treatment and storage. Eventhough, the majority (approximately 98%) of this styrene waste is styrene, utilization of this waste is limited due to large amount of anti-oxidant added and the presence of styrene oligomers which increase rapidly upon storage. The polystyrene plant of Thai Petrochemical Industry (TPI) Co.,Ltd. in Rayong province alone generates approximately 150 metric tons per month of styrene waste.

In order to solve this problem, a new way of effective utilizing of this styrene waste must be found. One way of this is, perhaps, the converting of styrene waste to 2-phenyl ethanol, the more useful and expensive product. The price of 2-phenyl ethanol is about 140 times higher than styrene waste, therefore, this idea is quite interesting commercially. 2-Phenyl ethanol is used as a fragrance in perfumery, cosmetics and toiletry products. The alcohol, as well as a number of its esters, has been isolated from a great variety of natural sources including oranges juice, *Plumeria acutifolia* oil, Japanese tobacco leaf oil, ylang-ylang, narcissus, hyacinth, lily, tea leaves, and rose. It possesses a remarkably pervasive rose odor that is not specially apparent in concentrated form. Traces of impurities markedly influence the flowery odor and render the alcohol without value as a perfumery material. The compound also undergoes the usual chemical reactions of alcohol or aromatic compounds.

The use of 2-phenyl ethanol presents no health problems. It has GARS status and has been approved for food used by the FDA. At present, 2-phenyl ethanol is obtained commercially from synthetic routes using various starting materials.

Objective

- 1) To investigate the possibility of synthesizing 2-phenyl ethanol from styrene waste.
- 2) To add value to styrene waste by converting it to the more expensive 2-phenyl ethanol.
- 3) To reduce the discharge of the styrene waste into environment by converting it to useful material.

Scope

- 1) To obtain optimum condition of the synthesizing of 2-phenyl ethanol from styrene in laboratory scale.
- 2) To conduct purification and verification of products obtained in the reaction.

Background

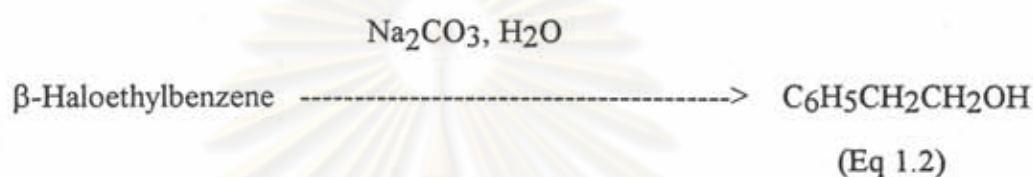
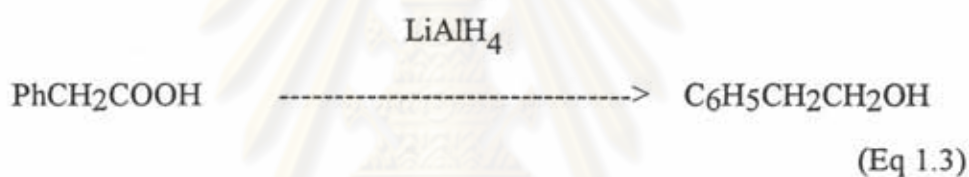
Although, 2-phenyl ethanol can be presently synthesized by various procedures, the most favorable method, is the Friedel-Crafts reaction between benzene and ethylene oxide [1]. In this reaction the only by-product is the hydrated aluminum chloride which can be used as a flocculating agent in municipal sewage-treatment installations.

Presently, there are many new methods of making 2-phenyl ethanol, for example,

1) Grignard synthesis [2,3]



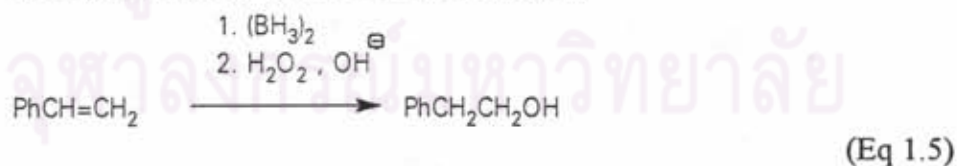
2) Hydrolysis of alkyl halides reaction [4]

3) Reduction reaction using LiAlH_4 [5]

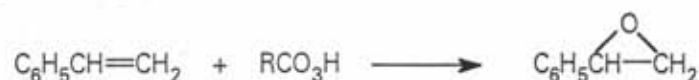
4) Reduction reaction of terminal olefin [6]



5) Hydroboration-oxidation reaction [7,8,9]



Method 4, the reduction reaction of terminal olefins, was used in this research. Styrene was first converted to styrene oxide by epoxidation reaction using percarboxylic acid.



(Eq 1.6)

Normally, percarboxylic acids used in epoxidation reaction are perbenzoic acid, m-chloroperbenzoic acid and monopercarboxyphthalic acid. Advantages of this method are the fact that acids are very active and large quantity of epoxide can be obtained. Moreover, the acids can react with most olefins. Peracetic acid and performic acid can also be used.

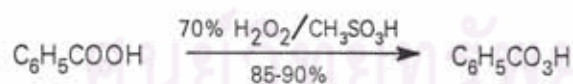
Percarboxylic acid can be synthesized by various methods, for example,

1) Synthesis of percarboxylic acid using benzoyl peroxides and sodium methoxides [10].



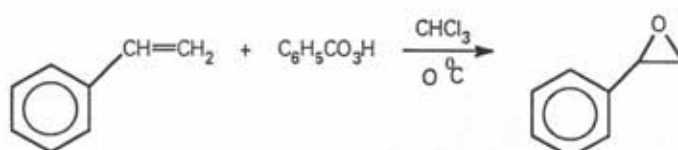
(Eq 1.7)

2) Synthesis of percarboxylic acid using benzoic acid and hydrogen peroxide with methane sulfonic acid as solvent. [11]



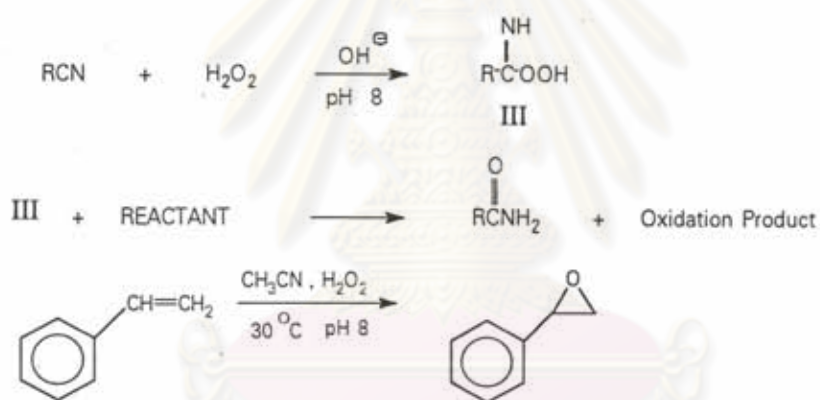
(Eq 1.8)

After the synthesis of perbenzoic acid, styrene oxide was normally synthesized as shown in equation 1.9 [12]. The synthesis of styrene oxide by this procedure gave yield of about 69-75%.



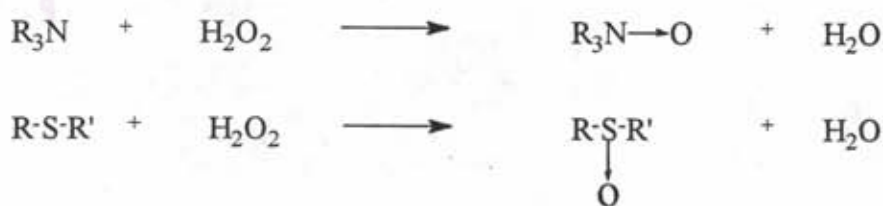
(Eq 1.9)

The other method of making styrene oxide was alkali-catalyzed epoxidation using nitrile as co-reactant. It was a new epoxidation technique that has been discovered recently. In this reaction, dilute hydrogen peroxide (30-50%) was utilized under essentially neutral condition. The procedure involves the initial reaction of an organic nitrile with hydrogen peroxide to produce what was most likely a peroxyoxycarboximidic acid. This new method has been successfully used to epoxidize cyclohexene and styrene resulting in 73 and 70 % yields of the corresponding epoxides, respectively. Equation 1.10 shows the reactions involved in this procedure [13]



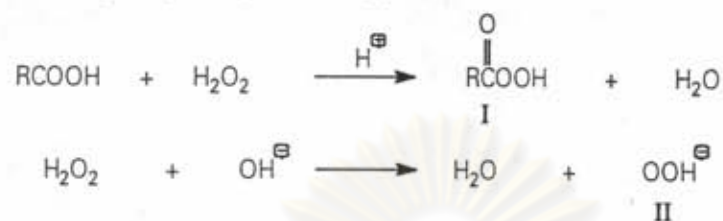
(Eq 1.10)

In general hydrogen peroxide was a poor oxidizing agent. Therefore, its use in organic reaction has generally been limited to the conversion of tertiary amines to their oxides and sulfides to sulfoxides:



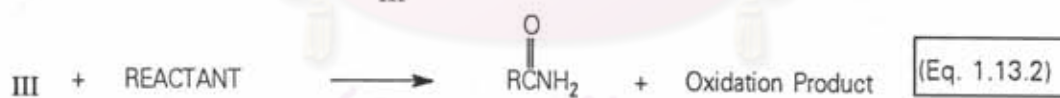
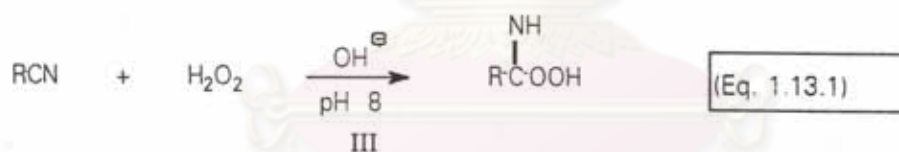
(Eq 1.11)

For other oxidation, including epoxidation and hydroxylation, the hydrogen peroxide must be "activated" by conversion to another species, usually as a peroxy acid (I) or the perhydroxyl anion (II).



(Eq 1.12)

A completely new method of achieving oxidation by hydrogen peroxide was developed through consideration of possible mechanisms involved in the epoxidation of acrylonitrile. In this system, hydrogen peroxide reacts with a nitrile under controlled pH condition (usually pH 8) to generate what believe to be a *peroxycarboximidic acid* intermediate (III). The latter has not been isolated; it reacted rapidly with any available reducing agents.



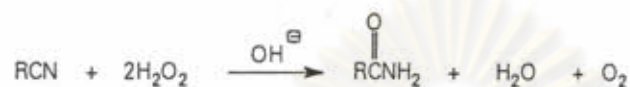
(Eq. 1.13)

In the absence of an added substrate (for example, an olefin), III reacts with hydrogen peroxide (now acting as reducing agent) to give amide and oxygen;



(Eq 1.14)

By adding together equations 1.13.1 and 1.13.2, one arrives at the classical expression for the hydrolysis of an organic nitrile by alkaline hydrogen peroxide ("Radziszewski Reaction"):



(Eq 1.15)

In the presence of a better reducing agent (for example, the olefin), reaction of III with hydrogen peroxide may often be eliminated and epoxidation of the olefin was accomplished instead.



(Eq 1.16)

It will be noted, of course, that regardless of how III reacts (Eq 1.14 or 1.16), it was converted to amide.

The reaction is not limited to epoxidation of ethylenic compounds. It can react with other functional groups, acetonitrile, for example, aniline is oxidized to azoxybenzene and pyridine to its N-oxide.

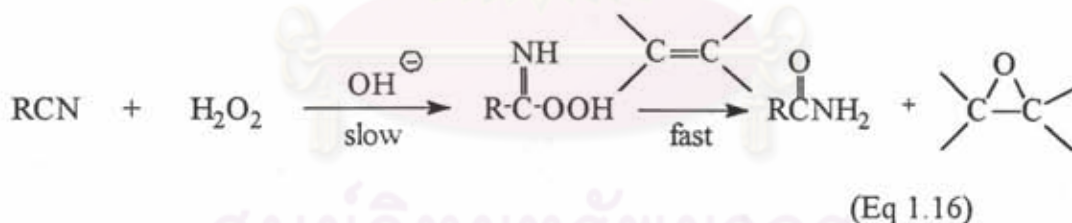
On the basis of the results obtained, certain conclusions are drawn regarding method of operation:

(a) *Optimum pH* is 7.5-8. At higher pH, oxygen evolution (measured by wet test meter) increases, indicating an increase hydrogen peroxide oxidation (Equation 3). This leads to a lower yield of epoxide.

(b) *Method of addition.* Hydrogen peroxide is best added slowly to an excess of both nitrile and olefin. This leads to a higher yields of epoxide, since reaction 2 is promoted at the expense of reaction 3.

(c) *Temperature.* This is not critical as long as proper pH, method of addition, and ratios of reactants are observed. Thus, equivalent yields (80-85% by titration of reaction mixtures for oxirane oxygen) are obtained at 60 °C as well as 35 °C.

Relative rates of epoxidation of 1-hexene and 2-methyl-2-butene. The rate of reaction of percarboxylic acid with an ethylenic compound was highly dependent upon the degree of substitution at double bond. For example, 2-methyl-2-butene is epoxidized by peroxyacetic acid at rate 290 times faster than that of 1-hexene. In contrast to the above result, the rate of disappearance of hydrogen peroxide, and olefins is essentially independent of olefin structure. This means that the slow step in the process has to be the formation of the peroxy carboximidic acid intermediate (III): this species must react rapidly with any available reducing agent.



Reaction of hydrogen peroxide with acetonitrile in the absence of base. In order to test the reactivity of hydrogen peroxide with acetonitrile in the absence of any added alkali, a solution of the former in the latter is allowed to reflux (68 °C) for 24 hours in the presence of added cyclohexene. Less than 5% of the peroxide reacts during that extended period.

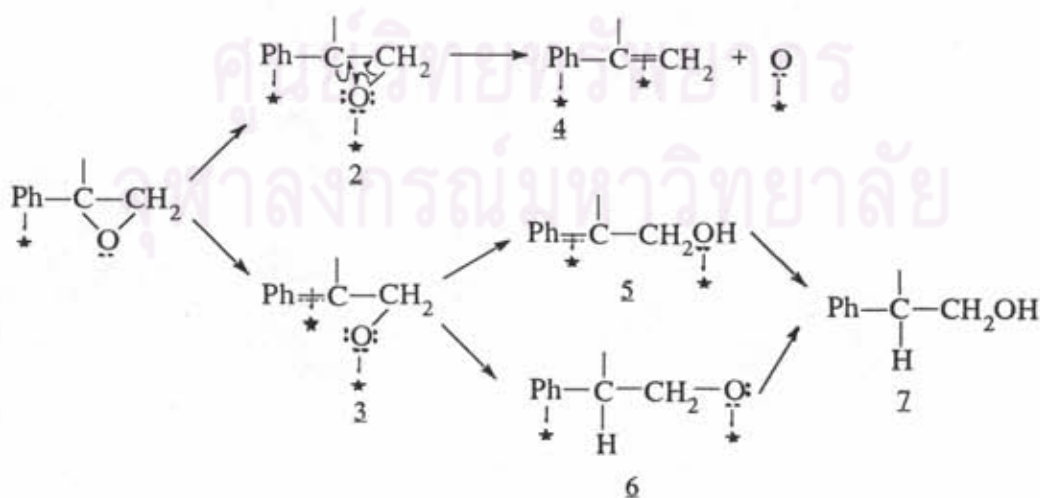
Epoxidation of ethylenic compounds. Styrene is oxidized using acetonitrile in methanol solution at 50 °C for four hours.

The catalytic hydrogenolysis of styrene oxides.

The styrene oxide could be converted to 2-phenyl ethanol by catalytic hydrogenolysis as in equation 1.17:



Deoxygenation has often been observed in the hydrogenolysis of epoxides(6). The hydrogenolysis of *p*-bromo- and 3,4-dichlorostyrene oxide over a PtO₂ give 1-phenyl ethanol as well as 2-phenyl ethanol, and the 1-phenyl ethanol undergoes corresponding hydrogenolysis to the corresponding ethylbenzene. However, styrene oxide and its *p*-methyl derivative are hydrogenolysed selectively to 2-phenyl ethanol. From these results, it is considered that the direction of ring-opening of epoxides by hydrogen was determined by the electronic effects of the substituents. On the other hand, more than 50% phenylcyclohexene is obtained from the Raney Ni catalyzed hydrogenolysis of 1-phenyl-7-oxabicyclo [4.1.0]heptane, and proposed a possible mechanism as in scheme 1.1.

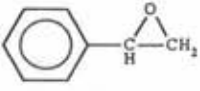
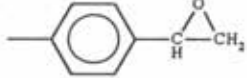
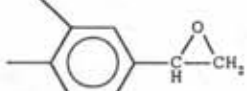
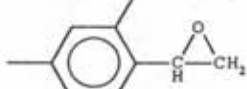
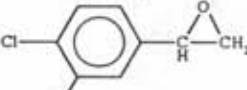
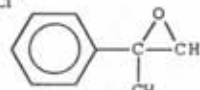


Scheme 1.1 The mechanism of deoxygenation reaction.

The data in table 1 summarize the hydrogenolysis of a series of styrene oxide (I-VI) over Raney Ni. These styrene oxides gave ethylbenzene (30-50%) as well as 2-phenyl ethanol, and scarcely any effect of substituents was observed. No 1-phenyl ethanol could be detected during the reactions in all cases. The competitive hydrogenation of an equimolar mixture of styrene oxide (I) and 1-phenyl ethanol also indicated that the amount of the latter compound was constant until I was consumed. Table 1 shows the dependence of the conversion on the deoxygenation in the hydrogenolysis of I. The deoxygenated products, ethylbenzene and styrene, were obtained significantly at the early stage of the reaction, and ethylbenzene was formed *via* styrene. The production of 2-phenyl ethanol increased as the reaction proceeded. A similar trend was also observed in the hydrogenolysis of *p*-methylstyrene oxide (II). These results eliminated the possibility that 1-phenyl ethanol was an intermediate of ethylbenzene, and indicated clearly that the deoxygenation of styrene oxides over Raney Ni proceeds *via* the corresponding styrene. The hydrogenolysis of optically active α -methylstyrene oxide (VI) occurred with slightly predominant retention of configuration. These deoxygenations could be explained by a previously proposed mechanism as shown in Scheme 1.1

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Table 1 The hydrogenolysis of styrene oxides over Raney Ni

Substrate	Catalyst ^a (g)	Products (%)	
		Ethylbenzene	2-phenylethanol
 (I)	0.05	23	77
	0.4	35	65
	1.0 ^b	56	44
	0.4 ^b	7	93
	0.4 ^c	12	88
 (II)	0.4	39	61
	0.4 ^e	13	87
 (III)	0.4	35	65
 (IV)	0.4	40	60
 (V)	0.4	50	50
 (VI)	0.4	36	64

Substrate: Four mmole. EtOH: 10 ml Under 1 ATM and 25 °C.

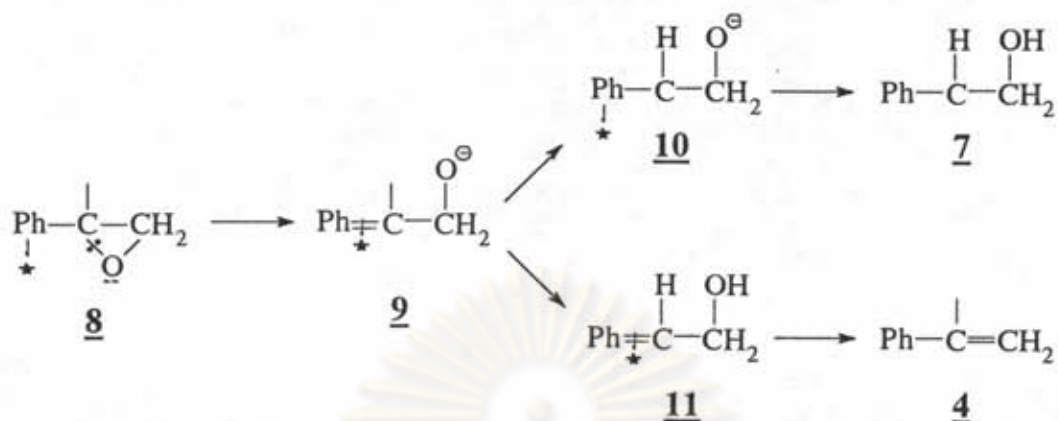
^aWet weight with EtOH. ^bUnder 100 ATM. ^cNaOH (1 mmole) was added. ^c = ^e

The strong adsorption of oxygen and phenyl groups increase the strain in the epoxy-ring, and the styrene oxide **1** will form the radical **2** as well as the π -benzyl complex **3**. The radical **2** will yield competitively the styrene **4** and the complex **3**. The significant deoxygenation in an early stage of the reaction indicates that the epoxide tends to cleave into the radical over fresh and active Raney Ni. As the reaction proceeds, the production of the radical will decrease because of aging of the catalyst. This consideration is supported by the fact that the deoxygenation is increased by increasing the amount of Raney Ni as shown in table 1. Moreover, the formation of the ethylbenzene under 100 ATM of hydrogen is lower than under 1 ATM. The Hydrogen addition to the radical or the nucleophilic

reaction becomes dominant rather than the formation of styrene as the hydrogen pressure increases.

The addition of sodium peroxide to the reaction decreased the formation of ethylbenzene, as shown in table 1. The hydrogenolysis of optically active VI proceeded with predominant inversion of configuration in the presence of sodium hydroxide on the catalyst surface that would decrease the adsorptivity of the epoxy-oxygen, and promoted the "SN 2" process, and, consequently, resulted in the decrease of deoxygenation.

The hydrogenolysis of styrene oxides (I-VI) yielded selectively 2-phenyl ethanol, scarcely any deoxygenation was observed. Optically active VI was hydrogenolysed predominantly to configurationally inverted 2-phenyl propanol. This result indicated that the hydrogenolysis of these styrene oxides also proceeded predominantly *via* "SN 2" process as shown in Scheme 2. However, the hydrogenolysis of 2-phenylpropane-1,2-diol, which involved the same π -benzyl complex 11, gave 2-phenylpropane (24%) as well as 2-phenyl propanol. Similar phenomena was observed in the hydrogenolysis of 1-phenyl-7-oxabicyclo-[4.1.0] heptane and 1-phenylcyclohexane-1,2-diol. Smith and Roth(6) described that a benzyl carbon metal bond will not achieve the maximum overlap because of π -complexing of phenyl to the surface, and the result of this effect is to increase the rate of the hydrogen addition to the complex. These facts indicated that the π -benzyl complex 9 will yield the alkoxide anion 10 rather than the π -benzyl complex 11.



Scheme 1.2 The hydrogenolysis of styrene oxides.

For hydrogenolysis reaction of styrene oxide, many catalysts such as Raney Ni, Pd, Pt can be used. Raney Ni will give around 50-90 % efficiencies depend on the condition of the synthesis. Pt and Pd will give more than 90% of 2-phenyl ethanol but it is more expensive than Raney Ni so it is not utilized in this study.

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