CHAPTER – 2

EXPERIMENTAL

The present chapter describes in detail the experimental methods for the synthesis of polymer supported ligands and metal complexes, characterization of newly synthesized catalysts and their catalytic activity.

2.1. SYNTHESIS

Materials

Chloromethylated poly (styrene-divinylbenzene) as spherical beads with 8% and 6% cross link (18-44 mesh, chlorine content = 17.5% and 16.5% respectively) were received from Ion Exchange India Limited, Mumbai. The chlorine content in the beads was estimated gravimetrically to ascertain the extent of chloromethylation [1]. Hydrated ruthenium trichloride ($RuCl_3.3H_2O$, Loba Chemie), L-valine (Merck), L-phenyl alanine (Merck), palladium chloride [Loba Chemie], Copper(II) acetate dihydrate [Merck] and Manganese(II) acetate tetrahydrate [Merck] were used as received. 1,4-dioxane, methanol, ethanol, acetonitrile and methylene dichloride (all AR grade) were purified by standard methods[1].

Synthesis of polymer anchored amino acids

Chloromethylated styrene-divinyl benzene copolymer beads were washed with a mixture of dioxane & water (50:50) followed by water and finally with methanol. The resin was carefully dried in an oven at 90°C for 8 h under vacuum.

Pre-washed and dried chloromethylated styrene-divinyl benzene copolymer beads (12g) in 35ml methanol were mixed with a solution of L-valine (9g) in 250ml distilled water

[L-phenyl alanine (12.5 g) in 350ml distilled water]. To this 6ml pyridine was added and contents refluxed for 16 h. The overall molar ratio of different reagents based on percent replaceable chlorine on resin approximately corresponds to 1: 1.25: 1.25 for Cl : amino acid : base. The contents were cooled and kept aside for one week with occasional shaking. At the end of this period, pH of the reaction mixture came down from the initial value of 7.1 to 5.1 while colour of the beads changed from off-white to pale yellow indicating the attachment of L-valine ligand. Finally the liganded polymer beads were filtered, washed with hot water followed by ethanol and dried under vacuum at 90°C for 8 h to yield 13.8 g of product.

In order to confirm the presence of free – COOH group after functionalization of L-valine through amino group on the polymer support, a known weight of the dry resin (8 % poly(S-DVB)L-val, 0.5 g) in 30ml of distilled water was refluxed for 10-12 h in presence of excess NaOH (10 ml, 0.1N) containing a few drops of phenolphthalein indicator. Upon cooling, the solution was filtered, washed carefully with 2 x 5 ml portions of water and the filtrate back titrated with 0.1N HCl. A simple calculation based on titre values showed that about 2.46% N equivalent to 1.76 mmol L-valine to be anchored per gram of polymer. In the case of 6% poly(S-DVB)L-val, this value was 2.43% N (1.74 mmol L-val/gm). Independently estimated nitrogen from microanalysis of the same samples (Table 2) gave values of 2.56 % N (1.83 mmol L-val/gm) and 2.47 % N (1.76 mmol L-val/gm) respectively. The close agreement of these results thus allowed us to quantify unambiguously the extent of amino acid loading on the cross-linked polymeric support.

Metal ion complexation with amino acid anchored resin

Liganded polymer beads (12.5 g) were kept in contact with ethanol (50 ml) for 45 min. To this was added an ethanolic solution (100 ml) of metal chloride (5 mmol) [metal acetate (5 mmol) containing 3 ml glacial acetic acid] and the contents gently agitated on a shaker at constant speed for 8 days at 25°C (pH = 2.5-3.5). The colour of the beads changed from pale yellow to light yellow in case of copper, grey in case of ruthenium, light brown in case of manganese and light brown in case of palladium during this period indicating formation of the metal complex on the polymer matrix. At the end of this period the coloured polymer was filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal chloride or metal acetate and dried in vacuum for 6h at 90°C.

Nomenclature/Description of Catalysts

The newly synthesized polymer anchored metal complex catalysts have been designated as under:

Mn A = 8% Poly(S-DVB)L-val Mn(II)
Mn B = 6% Poly(S-DVB)L-val Mn(II)

Ru A = 8% Poly(S-DVB)L-val Ru(III)
Ru B = 6% Poly(S-DVB)L-val Ru(III)

Cu A = 8% Poly(S-DVB)L-val Cu(II)
Cu B = 6% Poly(S-DVB)L-val Cu(II)

Pd A = 8% Poly(S-DVB)L-val Pd(II)
Pd B = 6% Poly(S-DVB)L-val Pd(II)

Mn C = 8% Poly(S-DVB)L-ph ala Mn(II)
Ru C = 8% Poly(S-DVB)L-ph ala Ru(III)

Cu C = 8% Poly(S-DVB)L-ph ala Cu(II)
Pd C = 8% Poly(S-DVB)L-ph ala Pd(II)

where,

8% & 6% denote percent cross link,
Poly(S-DVB) : poly(styrene-divinylbenzene)
L-val : L-valine
L-ph ala : L-phenyl alanine

2.2. CATALYST CHARACTERISATION

Elemental Analysis

The carbon, hydrogen and nitrogen present in the polymer bound metal complexes at various stages of preparation were determined using a Carlo-Erba Strumentazione microanalyser. The chlorine content in the chloromethylated poly(styrene-divinylbenzene) beads and that in the supported metal complexes were determined gravimetrically as silver chloride[1]. The Mn, Cu, Ru and Pd contents were determined as follows:

A known amount of the supported metal complex (0.2 gm) was digested with conc. HNO_3 (10 ml) for 12h, filtered and the filtrate diluted to 50ml in a volumetric flask with distilled water [2]. The solution was analysed using an Optima 4300DV Inductively Coupled Plasma Emission Spectrometer (Perkin Elmer).

Apparent Bulk Density

A typical procedure to determine the apparent bulk density of the polymer bound catalysts is described here:

In a 10ml graduated measuring cylinder weighed amount of catalyst was taken. The weighed catalyst in the cylinder was tapped for 250 times on a "Ceast Volumetric Classificator" with programmer and its volume measured when it remained constant after continuous tapping [3]. The experiment was repeated for three different weights and from the mean of three readings. the apparent bulk density was calculated using the equation:

$$\text{Apparent Bulk Density} = \frac{\text{Mass of the catalyst}}{\text{Volume of the catalyst bed}} \quad \text{(gm/ml)}$$

Surface Area and Pore volume

The texture (surface/mass, pore size, structure) of pure polymer supports and supported catalysts affects the rate of transport of reactants and products from the reaction centre. The adsorption - desorption isotherms of nitrogen were recorded on a Carlo-Erba surface analyzer series 1900 at liquid nitrogen temperature (-196°C) after degassing the sample for 4 h at 80°C. From the isotherms, the specific surface area and pore volume were calculated using BET [Brunett-Emmet-Teller] equation.

Swelling Studies

A systematic study on the swelling behaviour of the polymer support and the anchored complexes in aliphatic, aromatic, polar and nonpolar solvents were carried out using the following procedure [4].

Dried polymer supported catalyst (0.2 gm) was loaded into a glass filter tube fitted with a G_0 sintered disc and immersed into the solvent under study for 30 mins. The tube was then inserted into a 15ml centrifuge tube closed with a teflon cap and centrifuged for 15min. at 1200 rpm. The tube was immediately weighed and dried overnight at 100°C in a vacuum oven to constant weight. Using the difference in weights before and after drying, the mole percent of the swelling was calculated as :

$$\text{Swelling (S) (mole \%)} = \frac{C - D}{W \times M} \times 100$$

where C = weight of catalyst after centrifugation and before drying

D = weight of the catalyst after drying

W = weight of the catalyst

M = molecular weight of solvent under study

UV-Visible spectroscopy (DRS)

The UV-Visible reflectance spectra (200-800nm) of the solid catalysts were recorded on a Shimadzu UV-240 spectrophotometer and Perkin-Elmer UV-Vis-NIR Lambda 19 instrument with reference to a non-absorbing standard $BaSO_4$. Analyses of the catalysts were carried out by spraying the powdered catalyst on a $BaSO_4$ window to get a thin uniform layer.

Infra-red spectroscopy

The mid I.R (4000-400 cm^{-1}) and far I.R. (600-50cm^{-1}) spectra of the functionalised polymer i.e. supports at different stages of preparation and that of anchored metal complexes were recorded on a Nicolet Magna 550 FT-IR spectrophotometer as KBr pellets.

Scanning electron microscopy (SEM)

The morphology of the polymeric supports and the newly synthesized supported metal complexes were studied using CAMICA SU30 Scanning Electron Microscope with

SE electrode at 20 kV. The samples under study were sprayed on a double adhesive tape mounted on brass holder and coated with gold. The micrographs were recorded at 3 x 10^3 magnification.

Thermal stability studies

The analysis of the polymer supports and the anchored metal complex catalysts were studied in the temperature range of 50-600°C on a Shimadzu DT-30 instrument at a heating rate of 10°C min^{-1} under an atmosphere of nitrogen.

Electron Spin Resonance spectroscopy

Electron spin resonance spectra of polymer anchored metal complexes were recorded at room temperature on a Varian E112 spectrometer. TCNE was used as the 'g' marker.

2.3. CATALYTIC ACTIVITY

In the present work *epoxidation* of olefins such as styrene, norbornylene, *cis*-cyclooctene, cyclohexene ; *oxidation* of benzyl alcohol, cyclohexanol, toluene and cyclohexane were carried out using polymer supported metal complexes of Mn, Ru and Cu. *Hydrogenation* of 1-octene, cyclohexene, acetophenone and nitrobenzene were studied using supported Pd complexes.

Asymmetric epoxidation of straight chain unfuctionalized terminal olefins were also studied using polymer supported amino acid complexes of Mn, Ru and Cu. Asymmetric hydrogenation of acetophenone was similarly studied using Pd complexes.

Materials

The substrates, styrene (Merck), norbornylene (Aldrich), *cis*-cyclooctene (Aldrich), cyclohexene (Fluka), cyclohexane (Merck), toluene (Merck), benzyl alcohol (Merck), cyclohexanol (Fluka), 1-octene (Merck), acetophenone (Merck), nitro benzene (Merck) were used as received. Solvents and the other reagents were purified by literature methods [5]. TBHP (*tert*-butylhydroperoxide, 70% in water, Merck) was used as the terminal oxidant in the epoxidation/oxidation reactions. The strength of hydroperoxide was estimated by placing 2ml of glacial acetic acid and 25ml of isopropanol in a 250ml Erlenmeyer flask. To this 10ml of freshly prepared sodium iodide- isopropanol (prepared by refluxing a mixture of 22gms of NaI in 100ml of isopropanol) was added. An accurately measured sample of TBHP solution (containing not more than 2.5 mmol of active oxygen) was added and gently refluxed for 30 secs.

After dilution with 100ml of distilled water, the solution was titrated against 0.1N sodium thiosulphate till the disappearance of the yellow iodine colour using starch as the indicator [6]. The epoxidation/oxidation reactions were carried out under an atmosphere of high purity nitrogen. Hydrogenation reactions were carried out under high pressure of hydrogen gas.

Analysis of the reaction products

The analyses of various liquid products obtained in the catalytic oxidation/reduction reactions were carried out on Shimadzu 15A gas chromatograph using a 15% Carbowax column (1/8" x 2M) and Data lab GC 9000 using capillary columns AT-1 (0.32mm x 15M x 0.25μ thickness), attached to a flame ionization detector and N_2 as carrier gas. Product identification was also carried out on a Finnigan MAT 9001 GCQ-GC/MS system operated in the full scan mode and a quadrupole ion trap mass analyser. The Enantiomeric excesses (% ee) in the asymmetric epoxidation and reductions were determined Shimadzu 14B gas chromatograph using Chiraldex G-TA and Chiraldex A-TA columns (Astec 30 mts.).

Oxidation/Epoxidation of Olefins

The experimental set-up is shown in **Fig.2.3.1.** The oxidation/epoxidation of alcohols, alkanes/alkenes using polymer anchored catalysts **Mn A**, **Mn B**, **Ru A**, **Ru B**, **Cu A** and **Cu B** were carried out as per the following general procedure:

The catalyst (0.15 g) was initially allowed to swell in acetonitrile (20ml) for 30min in a two neck round bottom flask with a nitrogen inlet and a condenser. To this was added 5 mmol of the substrate followed by TBHP (10 mmol). A known amount of an internal standard (chlorobenzene, 60-80mg) was added to the above solution prior to the run. The flask was stoppered and the mixture stirred magnetically at different temperatures under a blanket of nitrogen taking care to avoid any loss of solvent vapours during agitation. Aliquots (~1µL) of reaction mixture were carefully withdrawn at regular intervals and the progress of the reaction monitored by GC. Representative chromatograms are shown in **Figs. 2.3.2 - 2.3.3**. Oxidation/epoxidation of alkanes and olefins did not take place in the absence of the catalyst. Peak positions of various reaction products were compared and matched with the retention times of authentic samples. Product profile of oxidation of different substrates is shown in **Schemes 2.3.1-2.3.2.**

Hydrogenation of 1-octene, cyclohexene, acetophenone and nitro benzene

High pressure catalytic hydrogenation reactions were carried out at 50°C in a 160ml Parr reactor (Model 4561) attached to a temperature controller (Model 4842) [**Plate 2.3.1**]. Substrate (10mmol), solvent methanol (30ml) and catalyst (100mg) were charged into the reactor. The reactor was pressurized with hydrogen in the range of 200psi to 500psi. The contents were stirred for 6 hours till no further drop in hydrogen pressure was noticed. The progress of the reaction was monitored by the fall in hydrogen pressure. After 6hrs, the reactor was cooled to room temperature, product separated from the catalyst by filtration and the filtrate analysed by GC as described above. A representative chromatogram of hydrogenation reaction is shown in **Fig.2.3.4.** A product profile of hydrogenation of different substrates is shown in **Scheme 2.3.3**.

High pressure kinetics

To understand the effects of hydrogen pressure on the reaction along with other operating parameters and to investigate in detail the kinetics of high pressure hydrogenation of 1-octene to n-octane following experiments were carried out.

The reaction was followed by recording the hydrogen pressure drop with time at different catalyst and substrate concentration and at different temperatures and H_2 pressures. As the total volume of solvent and substrate in the reactor was maintained constant in all the experiments, it is assumed that the concentration of hydrogen in the solution is proportional to the H_2 pressure at a constant stirring rate. Thus the ΔpH_2 values, which are proportional to the amount of n-octane produced, were calculated and these values were plotted as a function of time. This was also verified by analysing the actual conversions of 1-octene to n-octane periodically during the reaction time of 6h. Generally 15-20 min. was allowed for dissolution of H_2 and the dip tube inside the reactor was isolated prior to charging of the gas. We have applied the initial rate method for estimating the initial rate from the plot of $\Delta p(H_2)$ values (which is proportional to n-octane produced) as a function of time [7]. Making allowance for the initial induction period, initial rate r_i was determined from the slope of linear plot of ΔpH_2 (atm.) *vs.* time between 1-3 h. Conventional linear regression software was employed for all straight line fits.

Asymmetric epoxidation of unfuctionalized olefins

Asymmetric epoxidation of straight chain unfuctionalized terminal olefins were carried out using Mn, Ru and Cu catalysts as per the following procedure:

Alkene (1mmol), methylene dichloride (15 ml) and catalyst (100mg) (~0.18 mmol Mn/g resin; ~0.17 mmol Ru/g resin; ~0.45 mmol Cu/g resin) were charged into a 50 ml R.B. flask. Then *m*-CPBA (2 mmol) was slowly added in five equal portions over a period of 3 h. The reaction mixture was stirred for 10 hrs. at 25 °C. At the end of the reaction the catalyst was separated by filtration, filtrate washed with 1N NaOH (10ml) followed by distilled water. The product was finally extracted in methylene dichloride and dried over anhydrous sodium sulphate. This extract was analyzed by GC using chiral capillary column (Chiraldex ATA, 30 mtr.) to determine the percent optical yield. % ee was determined using following equation

$$\%\,\text{ee} \quad = \quad \frac{R-S}{R+S} \times 100$$

Asymmetric reduction of acetophenone

Asymmetric reduction of acetophenone was carried out under high pressure of H_2 using Pd catalysts at various temperatures (25, 40 & 50°C) in a 160ml Parr reactor as described earlier. Substrate (1mmol), solvent methanol (30ml), *t*-BuOK (0.3 g) and catalyst (100mg) were charged into the reactor. The reactor was pressurized with hydrogen in the range of 100psi to 400psi and contents stirred for 24 h. The product was separated from the catalyst by filtration and the filtrate analysed by GC. A representative chromatogram of asymmetric reduction is shown in **Fig.2.3.5.**

Catalysts recycle studies

Preliminary studies on recyclability of representative polymer supported catalysts were carried out in the oxidation/epoxidation of alcohols, alkanes and olefins.

In a representative procedure styrene as substrate, acetonitrile as solvent, TBHP as oxidant and PhCl as internal standard were employed. The reaction was carried out at 45°C for 24h. After the first cycle, the catalyst was carefully separated from the reaction mixture by filtration, washed with methanol and dried. The recovery was >98%. Fresh substrate and oxidants were charged in the subsequent cycles and the reaction continued for the same period. The products were analysed by GC at the end of each cycle. The experiments were extended to 4 cycles.

To study the recyclability of polymer supported catalysts in the hydrogenation of olefins, experiments were carried out at 50°C for a period of 6 h. 1-octene (10 mmol) was used as substrate with 10 mg of Pd catalyst & methanol as solvent (30ml). After each cycle the catalyst was filtered, washed with methanol and dried. The catalyst was recycled for 5 cycles.

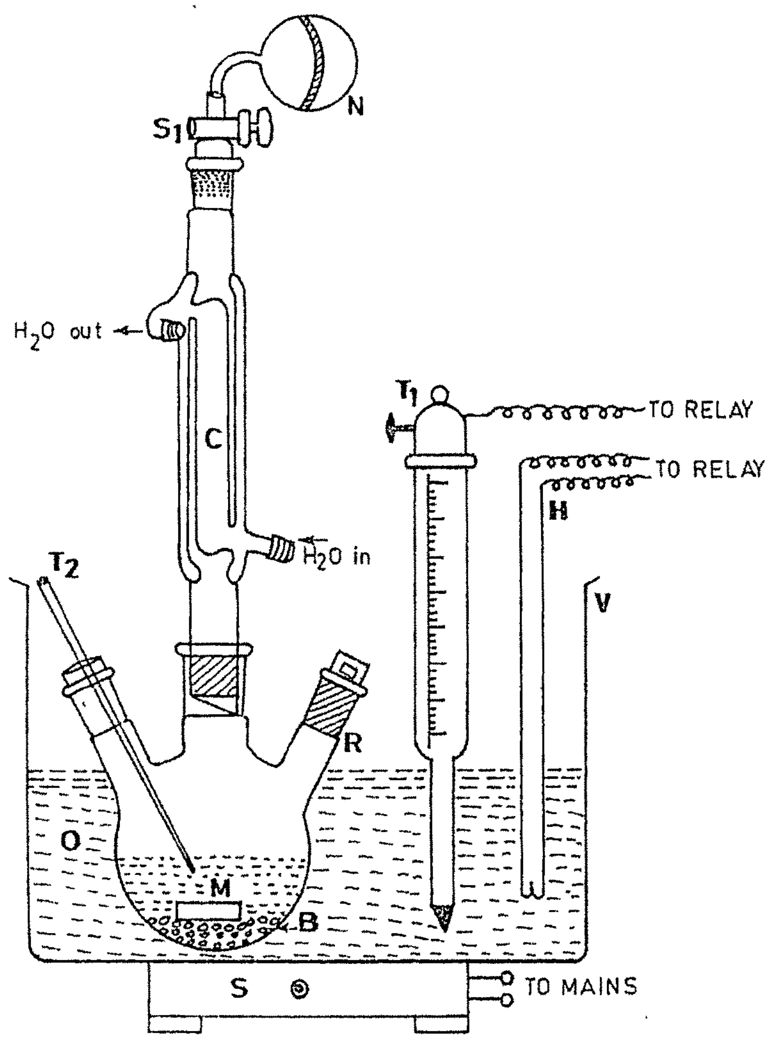


Fig. 1. EXPERIMENTAL SET-UP FOR EPOXIDATION OF OLEFINS

[C] Condenser(jacketed)
[N] Nitrogen balloon
[S_1] One way stopcock
[B] Catalyst beads
[O] Heating oil
[T_1] Contact thermometer
[H] Heating coil
[R] 3-necked Flask
[T_2] Thermometer
[M] Magnetic bar
[S] Stirrer
[V] Vessel

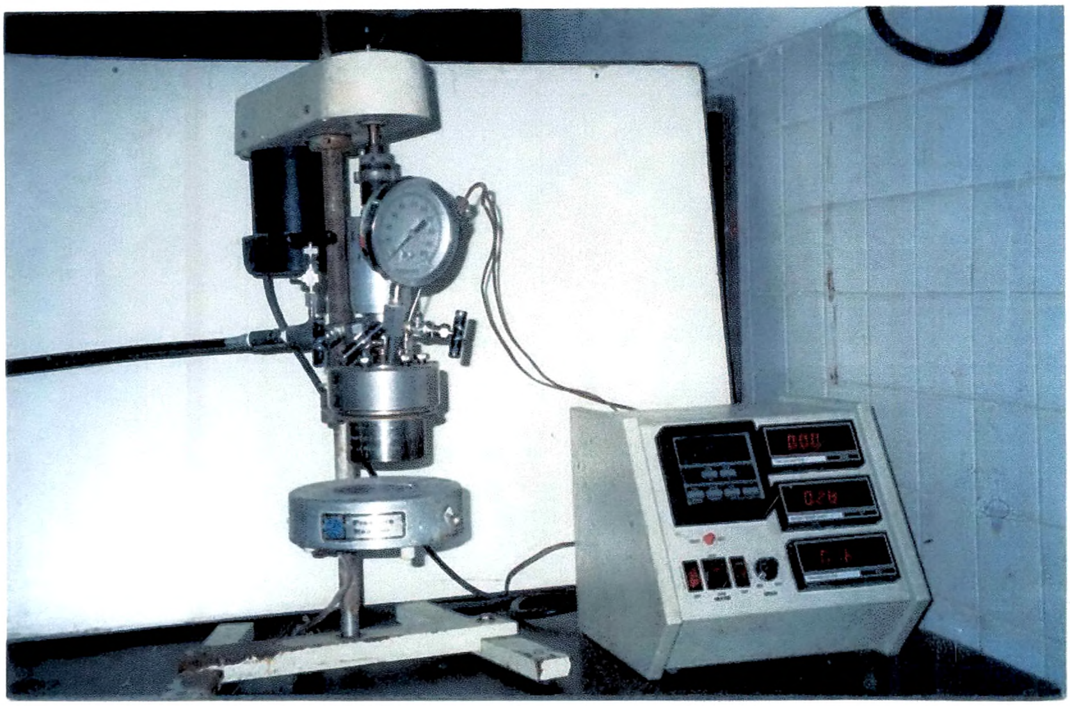
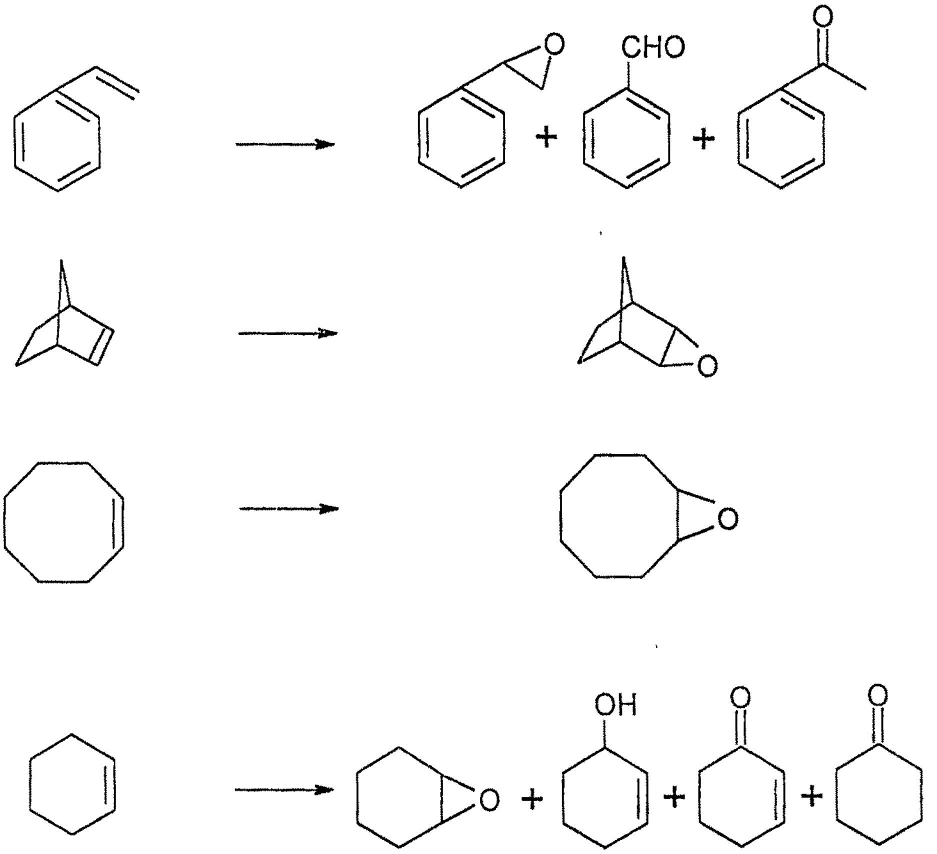
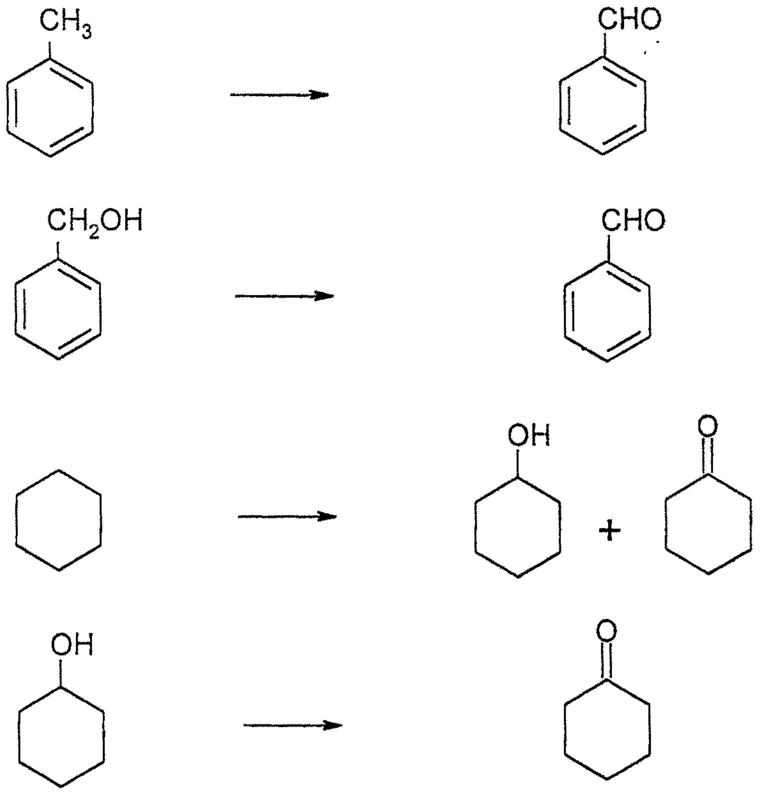


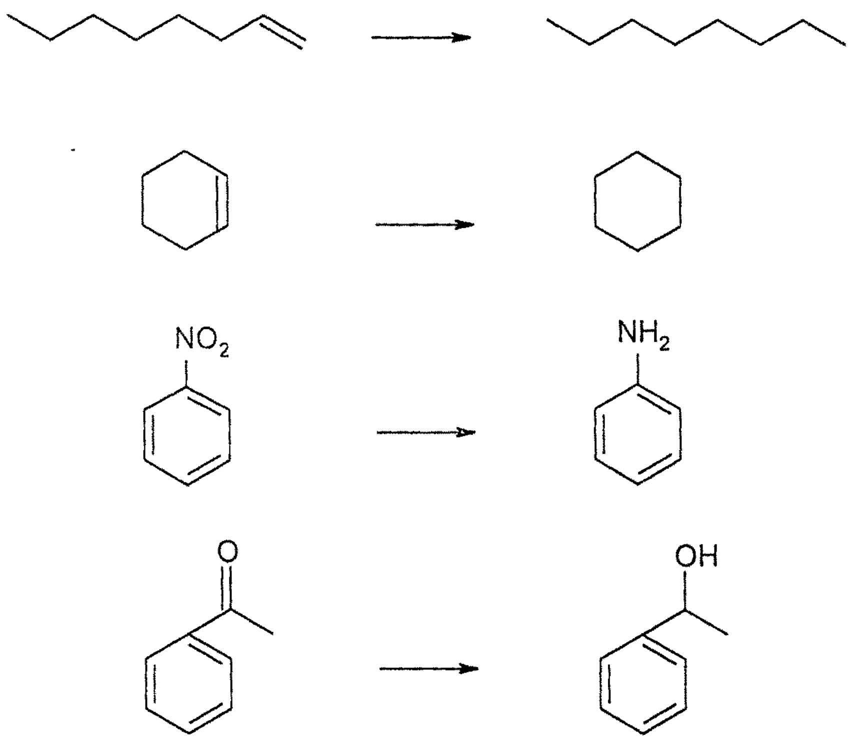
Plate 2.3.1 High pressure Parr reactor for hydrogenation reaction



Scheme 2.3.1 Epoxidation of different olefins using polymer supported catalysts.

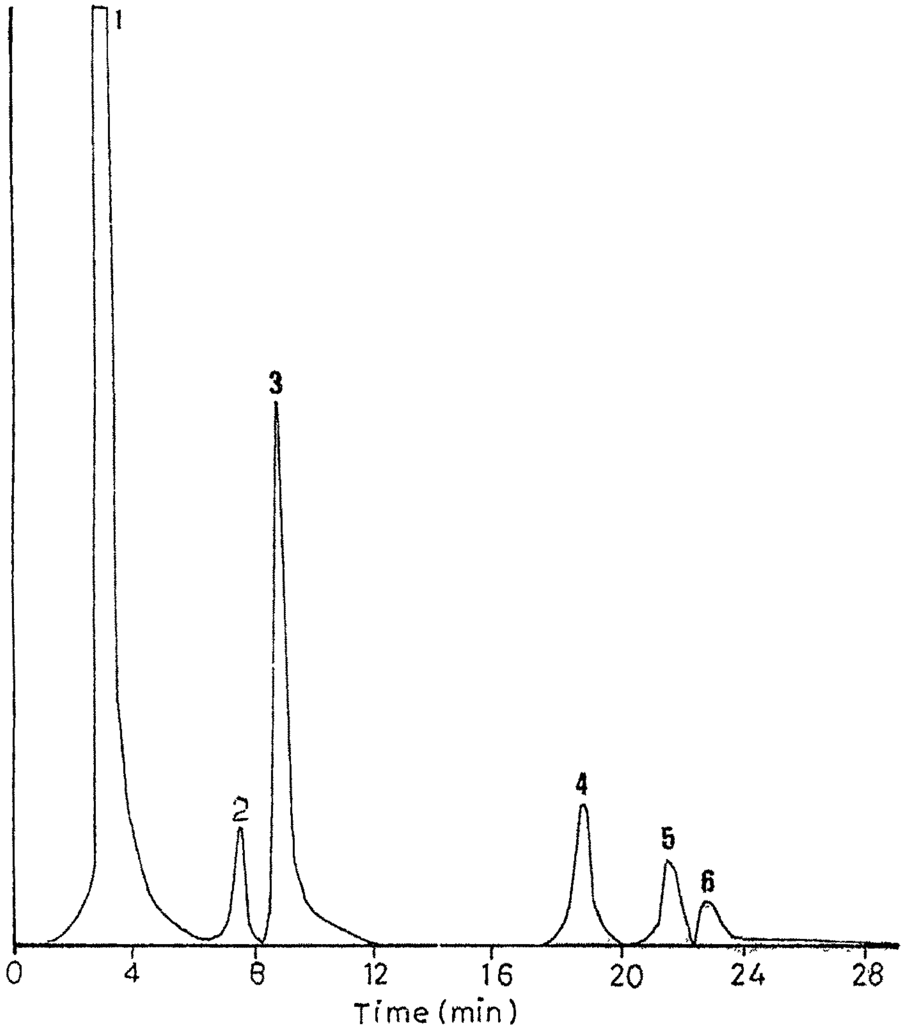


Scheme 2.3.2 Oxidation of different alkanes & alcohols using polymer supported catalysts.



Scheme 2.3.3 Hydrogenation of different substrates using polymer supported catalysts.

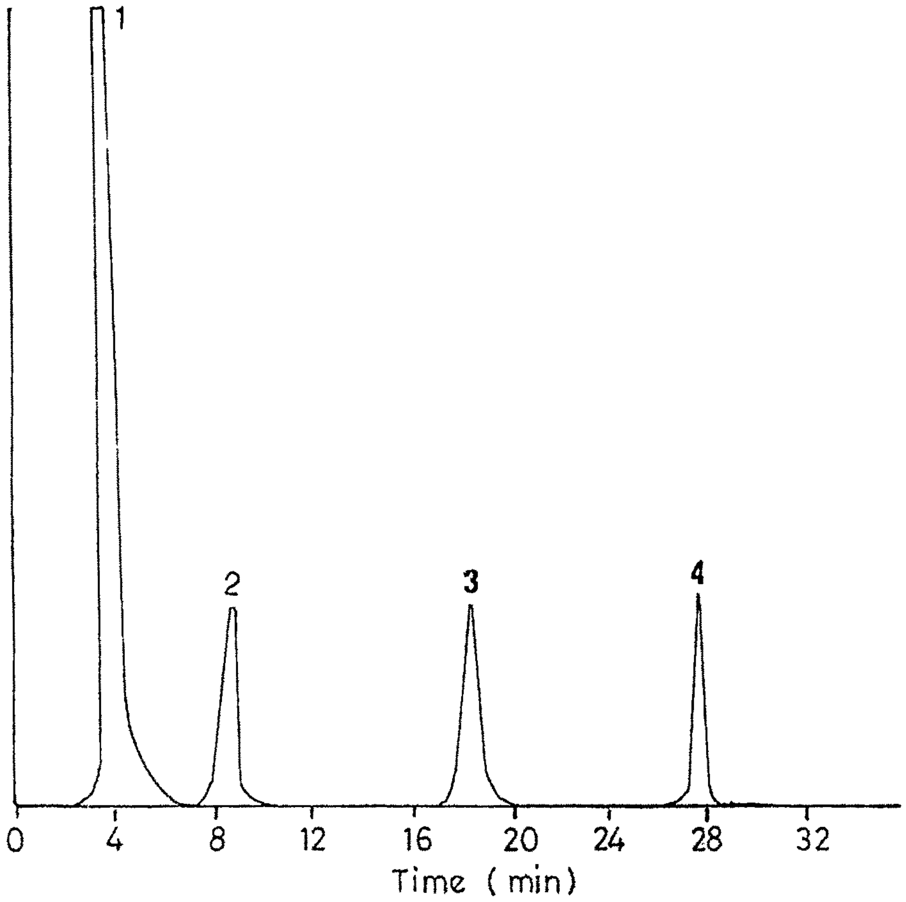
Column: 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector: Flame ionisation detector (FID)
Column temp. (initial): 80°C, **Column temp.** (final): 190°C
Detector temp.: 220°C, **Injection temp**: 210°C
Temp. Prog. (min) initial: 2 min.
Heating rate (°C/min): 4, **Range**: 10^2
Carrier gas: UHP Nitrogen, **Flow (ml/min)**: 30
Chart speed (mm/min): 5, **Sample size** (μl): 1.0



Identification: **1.** Acetonitrile (2.9); **2.** Chlorobenzene (7.5); **3.** Styrene (8.8); **4.** Benzaldehyde (18.4); **5.** Styrene oxide (21.5); **6.** Acetophenone (22.9).

Fig. 2.3.2 Typical GC analysis of epoxidation products of styrene.

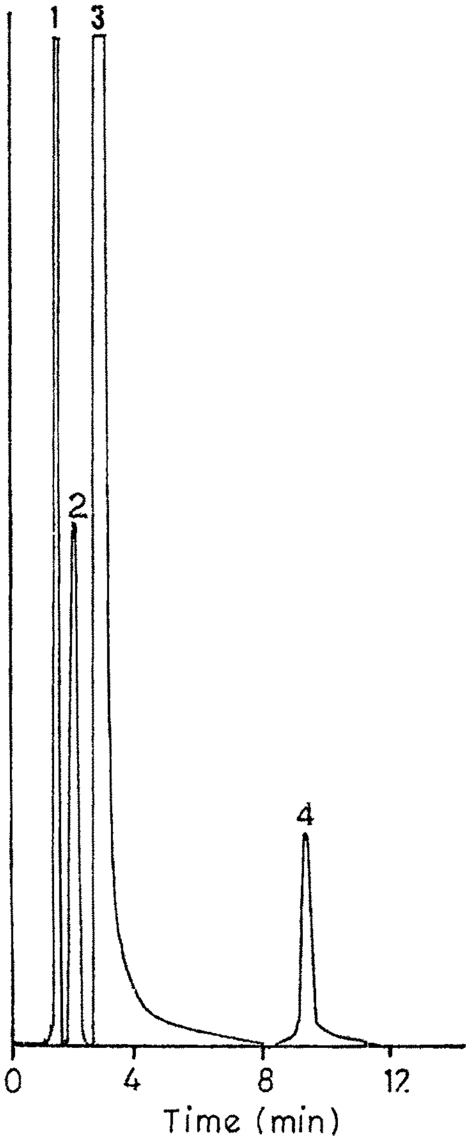
Column: 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector: Flame ionisation detector (FID)
Column temp. (initial): 80°C, **Column temp. (final)**: 200°C
Detector temp.: 220°C, **Injection temp**: 220°C
Temp. Prog. (min) initial: 2 min.
Heating rate (°C/min): 4, **Range**: 10^2
Carrier gas: UHP Nitrogen, **Flow (ml/min)**: 30
Chart speed (mm/min): 5, **Sample size (μl)**: 1.0



Identification: **1.** Acetonitrile (3.1); **2.** Chlorobenzene (7.8); **3.** Benzaldehyde (18.4); **4.** Benzyl alcohol(27.5)

Fig. 2.3.3 Typical GC analysis of oxidation products of benzyl alcohol.

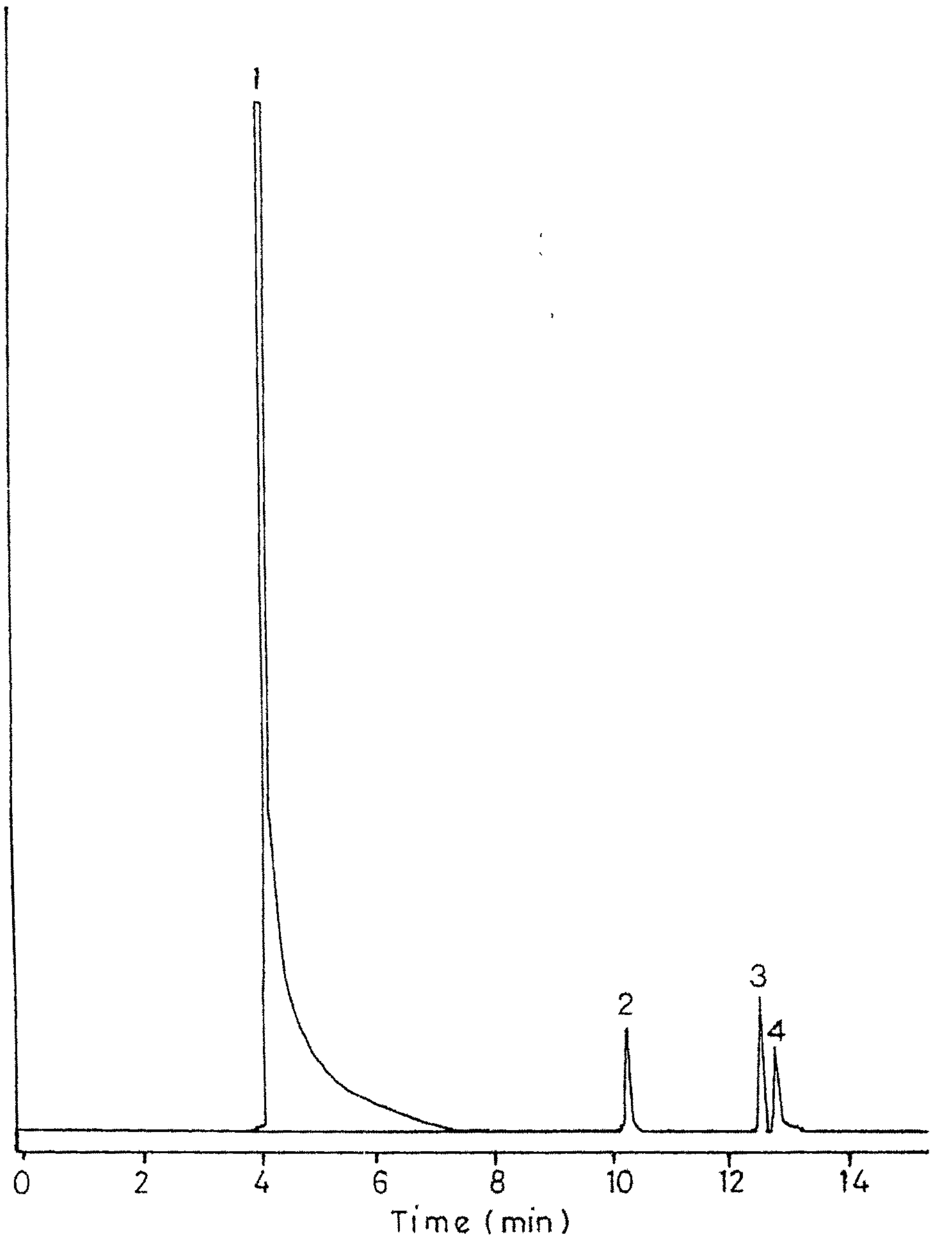
Column: 15% Carbowax on Chromosorb W(1/8" x 2 m)
Detector: Flame ionisation detector (FID)
Column temp. (initial): 60°C, **Column temp.** (final): 180°C
Detector temp.: 220°C, **Injection temp**: 210°C
Temp. Prog. (min) initial: 2 min.
Heating rate (°C/min): 4, **Range**: 10^2
Carrier gas: UHP Nitrogen, **Flow (ml/min)**: 30
Chart speed (mm/min): 5, **Sample size** (μl): 1.0



Identification: 1. n-Octane (1.5); **2.** 1-Octene (2.1); **3.** Methanol (3.0); **4.** Chlorobenzene (9.5).

Fig. 2.3.4 Typical GC analysis of hydrogenation products of 1-octene.

Column: Chiraldex GTA (astec) capillary (0.32mm x 30mts)
Detector: Flame ionisation detector (FID)
Column temp. : 120°C (Isothermal)
Detector temp.: 200°C, **Injection temp**: 200°C
Carrier gas: UHP Nitrogen, **Flow (kpa)**: 40
Chart speed (mm/min): 5, **Sample size (μl)**: 0.2



Identification: **1.** Methylene dichloride (4.0); **2.** Acetophenone (10.2); **3.** (R) 1-Phenyl ethanol (12.4); **4.** (S) 1-Phenyl ethanol (12.7).

Fig. 2.3.5 Typical GC analysis of asymmetric reduction products of acetophenone.

2.4. REFERENCES

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