

routes, properties, structure and reactivity, synthetic applications.

### UNIT - III:

[12 Hours]

**Transition metal-carbon pi complexes:** Preparative methods, nature of bonding, structural features of olefinic, acetylenic, allylic and  $\eta^5$ -cyclopentadienyl and  $\eta^6$ -benzene complexes. Important reactions relating to nucleophilic and electrophilic attack on ligands.

**Catalysis by organometallic compounds:** 16- and 18-electron rules, oxidative addition, insertion, deinsertion and reductive elimination reactions.

**Homogeneous catalysis by organometallics:** Hydrogenation, hydrosilation, hydrocyanation and isomerization of olefins, immobilisation of homogeneous hydrogenation catalysts, hydrocarbonylation of olefins (oxo reaction-cobalt and rhodium oxo catalysts), carbonylation of alcohols-Monsanto acetic acid process. Polymerization of olefins and acetylenes: Ziegler-Natta catalyst systems. Fischer-Tropsch reaction, Water Gas Shift reactions.

Synthetic applications of organocuprates. Hydrozirconation, transmetallation reactions by organonickels, carbonylation by metal carbonylates.

### References:

1. Chromatography-E. Heftman (Ed), Part A and Part B, 5<sup>th</sup> ed. Elsevier, 1992.
2. Chromatography Today- D. F. Poole and S.K. Poole, Elsevier, 1991.
3. Principles of Instrumental Analysis-Skoog, Holler and Nieman, 5<sup>th</sup> ed. Saunders, 1998
4. Quantitative Analysis-R. A. Day and A. L. Underwood, 5<sup>th</sup> ed. Prentice-Hall, 1998.
5. Instrumental Methods of Chemical Analysis -B. K. Sharma, 19<sup>th</sup> ed, Goel, 2000.
6. Principles and Applications of Organotransition Metal Chemistry - J.P.Collman, L.S.hegedus, J.R.Norton and R.G.Finke (University Science Books) 1987.
7. Organometallic Chemistry - R.C.Mehrotra and A.Singh (New Age International) 1999.
8. Organometallic Chemistry of Transition Metals-R.H.Crabtree (Wiley) 1999.

## OC S 556: Organic Synthetic Strategies and Petrochemicals

### COURSE OUTCOME:

Enable the students:

- To understand the preparation, properties and uses of polymer supported reagents in organic synthesis such as oligosaccharides, Dieckmann cyclisation, Aldol, Wittig, etherification, acetal formation and diazotransfer reactions.
- To gain the knowledge of mechanistic aspects of nine multicomponent reactions, asymmetric synthesis by employing chiral pool, chiral auxiliaries, chiral reagent and chiral catalysts.
- To learn the origin, formation and composition of petroleum, petroleum refining, reforming, fractionation, cracking, petroleum products and their applications,
- To learn manufacture of synthetic petrol, origin of coal, coal carbonization, coal gasification and coal tar based chemicals, coal conversions and manufacture of petrochemicals.

### UNIT- I:

[12 Hours]

**Polymer supported reagents in organic synthesis:** Introduction, properties of polymersupport, advantages of polymer supported reagents and choice of polymers. Applications: Substrate covalently bound to the support: Synthesis of oligosachcharides, Dieckmann cyclisation. Preparation of polymer bound aldehyde and application in aldol and Wittig reactions. Synthesis of polystyryl boronic acid and use in diol protection reaction. Reagent

linked to a polymeric material: Preparation of sulfonazide polymer and application in diazotransfer reaction. Synthesis of polymer bound per acid and its applications. Polymer supported catalytic reactions: Preparation of polymer supported  $AlCl_3$  and application in etherification and acetal formation reactions.

**Multicomponent Reactions:** Studies on the mechanistic aspects and use of the Ugi, Passerini, Biginelli, Hantzsch, Doebner-Miller, Jacobson, Barbier, Baylis-Hillmann and Mannich reactions.

## UNIT- II: [12 Hours]

**Assymmetric Synthesis:** The Chiral pool; Alpha amino acids in the synthesis of Benzodiazepines, Carbohydrates (Benzyl D-Mannose to Swainsonine) Preparation of tomolal from D-mannitol, Felion-Ahn model and Cram's chelation control. Enantiomeric excess and its determination.

**Chiral Auxiliaries:** Oxazolidinones, Chiral sulfoxides in controlling the reduction of ketones, Use of chiral Auxillaries in Diels-Alder and aldol reactions. **Chiral Reagents:** BINOL, DIBAL, Tartarates, Lithium diamides.

**Chiral Catalysts:** Rhodium and Ruthenium catalysts with Chiral phosphine ligands like (R)-BINAP, (R,R)-DIOP. Asymmetric amplification and autocatalysis.

## UNIT- III: [12 Hours]

**Petrochemicals:** Origin and formation of Petroleum, Composition of crude Petroleum and natural gas, Petroleum refining, reforming, fractionation, cracking, knocking, octane and cetane numbers. Ion, different types of petroleum products and their applications. Ignition point, flash point and octane number. Manufacture of synthetic petrol - Bergius and Fischer Tropsh processes.

Origin of coal, coal carbonisation, coal gasification and coal tar based chemicals. Chemistry of coal conversions.

**Manufacture of petrochemicals:** Preparation of methanol, chlorinated methanes and carbondisulphide from methane, Preparation of Ethyl chloride, ethanol, ethylene oxide from ethylene, manufacture of the following from propylene - Isopropanol, cumene, glycerine and acrylonitrile. Manufacture of vinyl chloride, chloroprene, acrylonitrile and acetaldehyde from acetylene.

### References:

1. Stereochemistry of Organic compounds-Nasipuri (New Age International).
2. Stereochemistry of Organic compounds-P.S. Kalsi (Wiley Eastern).
3. Organic chemistry- J. Clayden, N. Greeves, S. Warren and P. Wothers (Oxford University Press)
4. Stereochemistry of Organic compounds - E. Eliel and S.H. Wilen (John Wiley).
5. Art in Organic Synthesis- Anand, Bindra & Ranganath-(Wiley New Delhi), 1970.
6. Organic Synthesis a Disconnection Approach- Stuart Warren
7. Advanced Organic Chemistry-IV-Ed. Part A & B-F.J.Carrey & R.J.Sundberg (Kluwer) 2001.
8. Modern Methods of Organic Synthesis, 2<sup>nd</sup> edn.-N.Carruthers (Cambridge University), 1998.