

# VIJAYGARH JYOTISH RAY COLLEGE

## DEPARTMENT OF CHEMISTRY

NAME OF FACULTY – Dr SUMITA ROY

TOPIC – PORTION OF THE SYLLABUS COVERED FOR ALL SEMESTERS OF HONOURS PAPERS UNDER CBCS SYSTEM.

### SEMESTER 1(HONOURS)

#### **Stereochemistry I**

Bonding geometries of carbon compounds and representation of molecules: tetrahedral nature of carbon and concept of asymmetry; Fischer, sawhorse, flying wedge and Newman projection formulae and their inter translations. Concept of chirality and symmetry: symmetry elements, molecular chirality and centre of chirality; asymmetric and dissymmetric molecules; enantiomers and diastereomers; concept of stereogenicity, chirotopicity and pseudoasymmetry; chiral centres and number of stereoisomerism: systems involving 1/2/3-chiral centre(s) (AA, AB, ABA and ABC types). Relative and absolute configuration: D/L and R/S descriptors; erythro/threo and meso nomenclature of compounds; syn/anti nomenclatures for aldols; E/Z descriptors for C=C, conjugated diene, triene, C=N and N=N systems; combination of R/S- and E/ Z isomerisms. Optical activity of chiral compounds: optical rotation, specific rotation and molar rotation; racemic compounds, racemisation (through cationic, anionic, radical intermediates and through reversible formation of stable achiral intermediates); resolution of acids, bases and alcohols via diastereomeric salt formation; optical purity and enantiomeric excess; invertomerism of chiral trialkylamines.

#### **General Treatment of Reaction Mechanism II**

Reactive intermediates: carbocations (carbenium and carbonium ions), non-classical carbocations, carbanions, carbon radicals, carbenes: generation and stability, structure using orbital picture and electrophilic/nucleophilic behavior of reactive intermediates (elementary idea).

## SEMESTER 2(HONOURS)

### **Stereochemistry II**

Chirality arising out of stereoaxis: stereoisomerism of substituted cumulenes with even and odd number of double bonds; chiral axis in allenes, spiro compounds, alkylidenecycloalkanes and biphenyls; related configurational descriptors (R<sub>a</sub>/S<sub>a</sub>); atropisomerism; racemisation of chiral biphenyls. Concept of prostereoisomerism: prostereogenic centre; concept of (pro) n - chirality: topicity of ligands and faces (elementary idea); pro-R/pro-S, pro-E/pro-Z and R<sub>e</sub>/S<sub>i</sub> descriptors; pro-r and pro-s descriptors of ligands on propseudoasymmetric centre. Conformation: conformational nomenclature: eclipsed, staggered, gauche, syn and anti; dihedral angle, torsion angle; Klyne-Prelog terminology; P/M descriptors; energy barrier of rotation, concept of torsional and steric strains; relative stability of conformers on the basis of steric effect, dipole-dipole interaction and H-bonding; butane gauche interaction; conformational analysis of ethane, propane, n-butane, 2-methylbutane and 2,3-dimethylbutane; haloalkane, 1,2-dihaloalkanes and 1,2-diols (up to four carbons); 1,2-halohydrin; conformation of conjugated systems (s-cis and s-trans).

### **Nucleophilic substitution reactions**

Substitution at sp<sup>3</sup> centre [systems: alkyl halides, allyl halides, benzyl halides, alcohols, ethers, epoxides, α-halocarbonyls]: mechanisms (with evidence), relative rates & stereochemical features: S<sub>N</sub>1, S<sub>N</sub>2, S<sub>N</sub>2', S<sub>N</sub>1' (allylic rearrangement) and S<sub>N</sub>i; effects of solvent, substrate structure, leaving group and nucleophiles (including ambident nucleophiles, cyanide & nitrite); substitutions involving NGP (with hetero atoms and aryl groups); role of crown ethers and phase transfer catalysts.

## SEMESTER 3(HONOURS)

### **Electrophilic aromatic substitution**

Mechanisms and evidences in favour of it; orientation and reactivity; reactions: nitration, nitrosation, sulfonation, halogenation, Friedel-Crafts reaction; one-carbonelectrophiles (reactions: chloromethylation, 25 Gatterman-Koch, Gatterman, Houben-Hoesch, Vilsmeier-Haack, Reimer-Tiemann, Kolbe-Schmitt); Ipso substitution.

### **Nucleophilic Aromatic Substitution**

Addition-elimination mechanism and evidences in favour of it; SN1 mechanism; cine substitution (benzyne mechanism), structure of benzyne.

### **Exploitation of acidity of $\alpha$ -H of C=O**

Formation of enols and enolates; kinetic and thermodynamic enolates; reactions (mechanism with evidence): halogenation of carbonyl compounds under acidic and basic conditions, Hell-Volhard-Zelinsky (H. V. Z.) reaction, nitrosation, SeO<sub>2</sub> (Riley) oxidation; condensations (mechanism with evidence): Aldol, Tollens', Knoevenagel, Claisen-Schmidt, Claisen ester including Dieckmann, Stobbe; Mannich reaction, Perkin reaction, Favorskii rearrangement; alkylation of active methylene compounds; preparation and synthetic applications of diethyl malonate and ethyl acetoacetate; specific enol equivalents (lithium enolates, enamines and silyl enol ethers) in connection with alkylation, acylation and aldol type reaction.

### **Organometallics**

Grignard reagent; Organolithiums; Gilman cuprates: preparation and reactions (mechanism with evidence); addition of Grignard and organolithium to carbonyl compounds; substitution on -COX; directed ortho metalation of arenes using organolithiums, conjugate addition by Gilman cuprates; Corey-House synthesis; abnormal behaviour of Grignard reagents; comparison of reactivity among Grignard, organolithiums and organocopper reagents; Reformatsky reaction; Blaise reaction; concept of umpolung.

## SEMESTER 4(HONOURS)

### **Amines: Aliphatic & Aromatic**

Preparation, separation (Hinsberg's method) and identification of primary, secondary and tertiary amines; reaction (with mechanism): Eschweiler-Clarke methylation, diazo coupling reaction, formation and reactions of phenylenediamines, diazomethane and diazoacetic ester.

### **Nitro compounds (aliphatic and aromatic)**

Preparation and reaction (with mechanism): reduction under different conditions; Nef carbonyl synthesis, Henry reaction and conjugate addition of nitroalkane anion.

### **Alkyl nitrile and isonitrile**

Preparation and reaction (with mechanism): Thorpe nitrile condensation, von Richter reaction.

### **Diazonium salts and their related compounds**

Reactions (with mechanism) involving replacement of diazo group; reactions: Gomberg, Meerwein, Japp-Klingermann.

## **IR SPECTROSCOPY**

Introduction; modes of molecular vibrations (fundamental and non fundamental); IR active molecules; application of Hooke's law, force constant; fingerprint region and its significance; effect of deuteration; overtone bands; vibrational coupling in IR; characteristic and diagnostic stretching frequencies of C-H, N-H, O-H, C-O, C-N, C-X, C=C (including skeletal vibrations of aromatic compounds), C=O, C=N, N=O, C≡C, C≡N; characteristic/diagnostic bending vibrations are included; factors affecting stretching frequencies: effect of conjugation, electronic effects, mass effect, bond multiplicity, ring-size, solvent effect, H-bonding on IR absorptions; application in functional group analysis.

## **NMR Spectroscopy**

Introduction; nuclear spin; NMR active molecules; basic principles of Proton Magnetic Resonance; choice of solvent and internal standard; equivalent and non-equivalent protons; chemical shift and factors influencing it; ring current effect; significance of the terms: up-/downfield, shielded and deshielded protons; spin coupling and coupling constant (1st order spectra); relative intensities of first-order multiplets: Pascal's triangle; chemical and magnetic equivalence in NMR; anisotropic effects in alkene, alkyne, aldehydes and aromatics; NMR peak area, integration; relative peak positions with coupling patterns of common organic compounds (both aliphatic and benzenoid--aromatic); rapid proton exchange; interpretation of NMR spectra of simple compounds.

## SEMESTER 5(HONOURS)

### **HETEROCYCLIC COMPOUNDS**

Biological importance of heterocycles referred in the syllabus; 5- and 6-membered rings with one heteroatom; reactivity, orientation and important reactions (with mechanism) of furan, pyrrole, thiophene and pyridine; synthesis (including retrosynthetic approach and mechanistic details): pyrrole: Knorr synthesis, Paal-Knorr synthesis, Hantzsch; furan: Paal-Knorr synthesis, Feist-Benary synthesis and its variation; thiophenes: Paal-Knorr synthesis, Hinsberg synthesis; pyridine: Hantzsch synthesis; benzo-fused 5- and 6-membered rings with one heteroatom: reactivity, orientation and important reactions (with mechanistic details) of indole, quinoline and isoquinoline; synthesis (including retrosynthetic approach and mechanistic details): indole: Fischer, quinoline: Skraup, isoquinoline: Bischler-Napieralski synthesis.

### **Pericyclic reactions**

Mechanism, stereochemistry, regioselectivity in case of 39 Electrocyclic reactions: FMO approach involving  $4\pi$ - and  $6\pi$ -electrons (thermal and photochemical) and corresponding cycloreversion reactions. Cycloaddition reactions: FMO approach, Diels-Alder reaction, photochemical [2+2] cycloadditions. Sigmatropic reactions: FMO approach, sigmatropic shifts and their order; [1,3] and [1,5] H shifts and [3,3] shifts with reference to Claisen and Cope rearrangements.

### **Biomolecules**

**Amino acids:** synthesis with mechanistic details: Strecker, Gabriel; acetamido malonic ester, azlactone, Bücherer hydantoin synthesis, synthesis involving diketopiperazine, isoelectric point, zwitterions; electrophoresis, reaction (with mechanism): ninhydrin reaction, Dakin-West reaction; resolution of racemic amino acids. Peptides: peptide linkage and its geometry; syntheses (with mechanistic details) of peptides using N-protection & C-protection, solid-phase (Merrifield) synthesis; peptide sequence: C-terminal and N-terminal unit determination (Edman, Sanger and 'dansyl' methods); partial hydrolysis; specific cleavage of peptides; use of CNBr. Nucleic acids: pyrimidine and purine bases (only structure & nomenclature); nucleosides and nucleotides corresponding to DNA and RNA; mechanism for acid catalysed hydrolysis of nucleosides (both pyrimidine and purine types); comparison of alkaline hydrolysis of DNA and RNA; elementary idea of double helical structure of DNA (Watson-Crick model); complimentary base-pairing in DNA.

## SEMESTER 6( HONOURS)

### **Solvent extraction**

Classification, principle and efficiency of the technique. Mechanism of extraction: extraction by solvation and chelation. Technique of extraction: batch, continuous and counter current extractions. Qualitative and quantitative aspects of solvent extraction: extraction of metal ions from aqueous solution, extraction of organic species from the aqueous and nonaqueous media. Chromatography: Classification, principle and efficiency of the technique. Mechanism of separation: adsorption, partition & ion exchange. Development of chromatograms: frontal, elution and displacement methods. Qualitative and quantitative aspects of chromatographic methods of analysis: IC, GLC, GPC, TLC and HPLC. Stereoisomeric separation and analysis: Measurement of optical rotation, calculation of Enantiomeric excess (ee)/ diastereomeric excess (de) ratios and determination of enantiomeric composition using NMR, Chiral solvents and chiral shift reagents. Chiral chromatographic techniques using chiral columns (GC and HPLC). Role of computers in instrumental methods of analysis.

TOPIC – PRACTICAL SYLLABUS COVERED  
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**SEMESTER 1(HONOURS)**

**Separation** based upon solubility, by using common laboratory reagents like water (cold,hot), dil. HCl, dil. NaOH, dil. NaHCO<sub>3</sub>, etc., of components of a binary solid mixture; purification of any one of the separated components by crystallization and determination of its melting point. The composition of the mixture should be of the following types [ANY THREE]: p-Nitrobenzoic acid/p-Aminobenzoic acid; p Nitrotoluene/p-Anisidine; benzoic acid/naphthalene; urea/phenyl benzoate; p-toluidine/benzophenone; p-chlorobenzoic acid/ benzophenone, Benzoic acid/Anthracene; Glucose/Biphenyl; Benzoic acid/Benzophenone; Urea/Benzophenone. Use of pH paper is recommended.

**Determination of boiling point** of common organic liquid compounds [ANY FIVE]n butyl alcohol, cyclohexanol, ethyl methyl ketone, cyclohexanone, acetylacetone, isobutyl methyl ketone, isobutyl alcohol, acetonitrile, benzaldehyde and acetophenone. [Boiling points of the chosen organic compounds should preferably be within 1800 C]

**SEMESTER 2(HONOURS)**

**Organic Preparations**

A. The following reactions (any eight) are to be performed, noting the yield of the crude product:

1. Nitration of aromatic compounds
2. Condensation reactions
3. Hydrolysis of amides/imides/esters
4. Acetylation of phenols/aromatic amines
5. Brine mediated benzylation of amines/amino acids.
6. Side chain oxidation of aromatic compounds
7. Diazo coupling reactions of aromatic amines
8. Bromination of anilides using green approach (Bromate-Bromide method)
9. Redox reaction including solid-phase method
10. Green 'multi-component-coupling' reaction
11. Selective reduction of m-dinitrobenzene to m-nitroaniline

**Students must also calculate percentage yield, based upon isolated yield (crude) and theoretical yield.**

B. Purification of the crude product is to be made by crystallisation from water/alcohol, crystallization after charcoal treatment, or sublimation, whichever is applicable.

C. Melting point of the purified product is to be noted.

## SEMESTER 3(HONOURS)

### **A. Identification of a Pure Organic Compound**

**Solid compounds:** oxalic acid, tartaric acid, citric acid, succinic acid, resorcinol, urea, glucose, cane sugar, benzoic acid and salicylic acid.

**Liquid Compounds:** formic acid, acetic acid, methyl alcohol, ethyl alcohol, acetone, aniline, dimethylaniline, benzaldehyde, chloroform and nitrobenzene

### **B. Quantitative Estimations:**

Each student is required to perform all the experiments [ AnyFIVE will be set in the examination]

1. Estimation of glycine by Sørensen's formol method
2. Estimation of glucose by titration using Fehling's solution
3. Estimation of sucrose by titration using Fehling's solution
4. Estimation of aromatic amine (aniline) by bromination (Bromate-Bromide) method
5. Estimation of acetic acid in commercial vinegar
6. Estimation of urea (hypobromite method)
7. Estimation of saponification value of oil/fat/ester

## SEMESTER 4(HONOURS)

### **Experiment: Qualitative Analysis of Single Solid Organic Compounds**

1. Detection of special elements (N, S, Cl, Br) by Lassaigne's test
2. Solubility and classification (solvents: H<sub>2</sub>O, 5% HCl, 5% NaOH and 5% NaHCO<sub>3</sub>)
3. Detection of the following functional groups by systematic chemical tests: aromatic amino (-NH<sub>2</sub>), aromatic nitro (-NO<sub>2</sub>), amido (-CONH<sub>2</sub>, including imide), phenolic -OH, carboxylic acid (-COOH), carbonyl (distinguish between -CHO and >C=O); only one test for each functional group is to be reported.
4. Melting point of the given compound
5. Preparation, purification and melting point determination of a crystalline derivative of the given compound.
6. Identification of the compound through literature survey. Each student, during laboratory session, is required to carry out qualitative chemical tests for all the special elements and the functional groups with relevant derivatisation in known and unknown (at least six) organic compounds.



## SEMESTER 5(HONOURS)

### **A. Chromatographic Separations**

1. TLC separation of a mixture containing 2/3 amino acids
2. TLC separation of a mixture of dyes (fluorescein and methylene blue)
3. Column chromatographic separation of mixture of dyes
4. Paper chromatographic separation of a mixture containing 2/3 amino acids
5. Paper chromatographic separation of a mixture containing 2/3 sugars

### **B. Spectroscopic Analysis of Organic Compounds**

1. Assignment of labelled peaks in the  $^1\text{H}$  NMR spectra of the known organic compounds explaining the relative  $\delta$ -values and splitting pattern.
2. Assignment of labelled peaks in the IR spectrum of the same compound explaining the relative frequencies of the absorptions (C-H, O-H, N-H, C-O, C-N, C-X, C=C, C=O, N=O,  $\text{C}\equiv\text{C}$ ,  $\text{C}\equiv\text{N}$  stretching frequencies; characteristic bending vibrations are included).
3. The students must record full spectral analysis of at least 15 (fifteen) compounds from the following list:

(i) 4'-Bromoacetanilide (ii) 2-Bromo-4'-methylacetophenone (iii) Vanillin (iv) 2'-Methoxyacetophenone (v) 4-Aminobenzoic acid (vi) Salicylamide (vii) 2'-Hydroxyacetophenone (viii) 1,3-Dinitrobenzene (ix) trans-Cinnamic acid (x) Diethyl fumarate (xi) 4-Nitrobenzaldehyde (xii) 4'-Methylacetanilide (xiii) Mesityl oxide (xiv) 2-Hydroxybenzaldehyde (xv) 4-Nitroaniline (xvi) 2,3-Dimethylbenzotrile (xvii) Pent-1-yn-3-ol (xviii) 3-Nitrobenzaldehyde (xix) 3-Aminobenzoic acid (xx) Ethyl 3-aminobenzoate (xxi) Ethyl 4-aminobenzoate (xxii) 3-nitroanisole.

TOPIC – PORTION OF SYLLABUS COVERED FOR SEMESTER 4  
GENERAL(THEORY)  
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### **Alcohols, Phenols and Ethers**

Alcohols: (up to 5 Carbons). Preparation: 1°-, 2°- and 3°- alcohols: using Grignard reagent, reduction of aldehydes, ketones, carboxylic acid and esters; Reactions: With sodium, oxidation (alkaline  $\text{KMnO}_4$ , acidic dichromate).

Diols: Pinacol- pinacolone rearrangement (with mechanism) (with symmetrical diols only).

Phenols: Preparation: cumene hydroperoxide method, from diazonium salts; acidic nature of phenols; Reactions: electrophilic substitution: nitration and halogenations; Reimer -Tiemann reaction, Schotten -Baumann reaction, Fries rearrangement and Claisen rearrangement. Ethers: Preparation: Williamson's ether synthesis; Reaction: cleavage of ethers with HI.

### **Amines and Diazonium Salts**

Amines (aliphatic and aromatic): strength of organic bases; Preparation: from alkyl halides, Hofmann degradation; Reactions: with  $\text{HNO}_2$  (distinction of 1°-, 2°- and 3°- amines), Schotten - Baumann reaction, Diazo coupling reaction (with mechanism).

Diazonium salts: Preparation: from aromatic amines; Reactions: conversion to benzene, phenol, benzoic acid and nitrobenzene. Nitro compounds (aromatic): reduction under different conditions (acidic, neutral and alkaline).

### **Carbohydrates:**

classification and general properties; glucose and fructose: constitution; osazone formation; oxidation-reduction reactions; ascending (Kiliani -Fischer method) and descending (Ruff's method) in monosaccharides (aldoses only); mutarotation

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### **Carbonyl Compounds**

Aldehydes and Ketones (aliphatic and aromatic): (Formaldehyde, acetaldehyde, acetone and benzaldehyde): Preparation: from acid chlorides, from nitriles and from Grignard reagents; general properties of aldehydes and ketones; Reactions: with  $\text{HCN}$ ,  $\text{NaHSO}_3$ ,  $\text{NH}_2\text{-G}$  derivatives and with Tollens' and Fehling's reagents; iodoform test; aldol condensation (with mechanism); Cannizzaro reaction (with mechanism), Wittig reaction, benzoin condensation; Clemmensen reduction, Wolff- Kishner reduction

## **Carboxylic Acids and Their Derivatives**

Carboxylic acids (aliphatic and aromatic): strength of organic acids: comparative study with emphasis on factors affecting pK values; Preparation: acidic and alkaline hydrolysis of esters (BAC2 and AAC2 mechanisms only) and from Grignard reagents. Carboxylic acid derivatives (aliphatic): (up to 5 carbons). Preparation: acid chlorides, anhydrides, esters and amides from acids; Reactions: Interconversion among acid derivatives. Reactions: Claisen condensation; Perkin reaction.

## **Amino Acids**

Amino Acids: Preparations (glycine and alanine only): Strecker synthesis, Gabriel's phthalimide synthesis; general properties; zwitterion, isoelectric point.

## **TOPIC – PRACTICAL SYLLABUS COVERED FOR SEMESTER 4 (GENERAL)**

**FACULTY NAME – Dr SUMITA ROY & Dr ANINDITA MUKHERJEE**

### **1. Qualitative Analysis of Single Solid Organic Compound(s)**

Experiment A: Detection of special elements (N, Cl, and S) in organic compounds.

Experiment B: Solubility and Classification (solvents: H<sub>2</sub>O, dil. HCl, dil. NaOH)

Experiment C: Detection of functional groups: Aromatic-NO<sub>2</sub>, Aromatic -NH<sub>2</sub>, -COOH, carbonyl (no distinction of -CHO and >C=O needed), -OH (phenolic) in solid organic compounds. Experiments A - C with unknown (at least 6) solid samples containing not more than two of the above type of functional groups should be done.

### **2. Identification of a pure organic compound**

Solid compounds: oxalic acid, tartaric acid, succinic acid, resorcinol, urea, glucose, benzoic acid and salicylic acid.

Liquid Compounds: methyl alcohol, ethyl alcohol, acetone, aniline, dimethylaniline, benzaldehyde, chloroform and nitrobenzene