WEST BENGAL STATE UNIVERSITY

SYLLABUS IN CHEMISTRY (HONOURS)
ORGANIC CHEMISTRY PORTION
UNDER CBCS

SEMESTER 1, 3 AND 5

(This is the modified syllabus only for the academic session 2020-21 for the above-mentioned semesters in view of the COVID pandemic as per resolution taken in the UGBOS meetings of the Department of Chemistry)

This document contains a total of 9 pages

CORE COURSE (HONOURS) IN CHEMISTRY

SEMESTER-I

CEMACOR01T: **ORGANIC CHEMISTRY-I**

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures **Marks: 50**

Basics of Organic Chemistry Bonding and Physical Properties
(25 Lectures) **Marks: 20**

Valence Bond Theory: concept of hybridisation, shapes of molecules, resonance (including hyperconjugation); calculation of ~~formal charges and~~ double bond equivalent (DBE); orbital pictures of bonding (sp^3, sp^2, sp: C-C, C-N & C-O systems ~~and *s-cis* and *s-trans* geometry for suitable cases)~~.

Electronic displacements: inductive effect, ~~field effect~~, mesomeric effect, resonance energy; bond polarization and bond polarizability; electromeric effect; steric effect, ~~steric inhibition of resonance~~. steric inhibition of rsonance

MO theory: qualitative idea about molecular orbitals, ~~bonding and antibonding interactions~~, idea about σ, σ^*, π, π^*, n – MOs; ~~basic idea about Frontier MOs (FMO)~~; concept of HOMO, LUMO and SOMO; interpretation of chemical reactivity in terms of FMO interactions; sketch and energy levels of π MOs of i) acyclic p orbital system (C=C, conjugated diene, triene, allyl and pentadienyl systems) ~~ii) cyclic p orbital system (neutral systems: [4], [6] annulenes; charged systems: 3-,4-,5-membered ring systems)~~; Hückel's rules for aromaticity up to [10]-annulene (including mononuclear heterocyclic compounds up to 6-membered ring); concept of antiaromaticity and homoaromaticity; non-aromatic molecules; Frost diagram; ~~elementary idea about α and β; measurement of delocalization energies in terms of β for buta-1,3-diene, cyclobutadiene, hexa-1,3,5-triene and benzene~~.

Physical properties: influence of hybridization on bond properties: bond dissociation energy (BDE) and bond energy; bond distances, bond angles; concept of bond angle strain (Baeyer's strain theory); ~~melting point~~/boiling point and solubility of common organic compounds in terms of ~~covalent &~~ non-covalent intermolecular forces; polarity of molecules and dipole moments; relative stabilities of isomeric hydrocarbons in terms of heat of hydrogenation, heat of combustion ~~and heat of formation~~.

General Treatment of Reaction Mechanism I
(10 Lectures) **Marks: 10**

Mechanistic classification: ionic, radical and pericyclic (definition and example); reaction type: addition, elimination and substitution reactions (definition and example); nature of bond cleavage and bond formation: homolytic and heterolytic bond fission, homogenic and heterogenic bond formation; curly arrow rules in representation of mechanistic steps; reagent type: electrophiles and nucleophiles (elementary idea); electrophilicity and nucleophilicity in terms of FMO approach.
Reactive intermediates: carbocations (carbenium and carbonium ions), carbanions, carbon radicals, carbenes: generation and stability, structure using orbital picture and electrophilic/nucleophilic behavior of reactive intermediates (elementary idea).

Stereochemistry I
(25 Lectures) **Marks: 20**

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.

and point group: Cnh, Cnv, Dnh

Concept of chirality and symmetry: symmetry elements and point groups ($C_{\infty v}$, C_{nh}, C_{nv}, C_n, $D_{\infty h}$, D_{nh}, D_{nd}, D_n, S_n(C_s, C_i); molecular chirality and centre of chirality; asymmetric and dissymmetric molecules; enantiomers and diastereomers; concept of epimers; 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.

***CEMACOR01P:* ORGANIC CHEMISTRY-I LAB**
(60 Lectures/Contact Hours) **Marks: 25**

1. Separation, based upon solubility, by using common laboratory reagents like water (cold, hot), dil. HCl, dil. NaOH, dil. $NaHCO_3$, *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 may be of the following types: Benzoic acid/*p*-Toluidine; *p*-Nitrobenzoic acid/*p*-Aminobenzoic acid; *p*-Nitrotoluene/*p*-Anisidine; *etc*.

2. Determination of boiling point of common organic liquid compounds e.g., ethanol, cyclohexane, chloroform, ethyl methyl ketone, cyclohexanone, acetylacetone, anisole, crotonaldehyde, mesityl oxide, *etc*. [Boiling point of the chosen organic compounds should preferably be less than 160 °C]

3. **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

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SEMESTER-III

CEMACOR07T: ORGANIC CHEMISTRY-III

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Chemistry of alkenes and alkynes
(15 Lectures) Marks: 12

Addition to C=C: mechanism (with evidence wherever applicable), reactivity, regioselectivity (Markownikoff and anti-Markownikoff additions) and stereoselectivity; reactions: hydrogenation, halogenations, iodolactonisation, hydrohalogenation, hydration, oxymercuration-demercuration, hydroboration-oxidation, epoxidation, *syn* and *anti*-hydroxylation, ozonolysis, addition of singlet and triplet carbenes; electrophilic addition to diene (conjugated dienes and allene); radical addition: HBr addition; mechanism of allylic and benzylic bromination in competition with brominations across C=C; use of

NBS; Birch reduction of benzenoid aromatics; interconversion of *E* - and *Z* - alkenes; ~~contra thermodynamic isomerization of internal alkenes~~.

Addition to C≡C (in comparison to C=C): mechanism, reactivity, regioselectivity (Markownikoff and anti-Markownikoff addition) and stereoselectivity; reactions: hydrogenation, halogenations, hydrohalogenation, hydration, ~~oxymercurationdemercuration~~, hydroboration-oxidation, dissolving metal reduction of alkynes (Birch); reactions of terminal alkynes by exploring its acidity; interconversion of terminal and non-terminal alkynes.

Aromatic Substitution
(10 Lectures) Marks: 08

*Electrophilic aromatic substitution:*mechanisms and evidences in favour of it; orientation and reactivity; reactions: nitration, nitrosation, sulfonation, halogenation, Friedel-Crafts reaction; one-carbon electrophiles (reactions: ~~chloromethylation, Gatterman-Koch, Gatterman, Houben-Hoesch~~, Vilsmeier-Haack, Reimer-Tiemann, Kolbe-Schmidt); *Ipso* substitituion.

Nucleophilic aromatic substitution: addition-elimination mechanism and evidences in favour of it; ~~S_N1 mechanism~~; cine substitution (benzyne mechanism), structure of benzyne.

Carbonyl and Related Compounds
(30 Lectures) Marks: 22

Addition to C=O: structure, reactivity and preparation of carbonyl compounds; mechanism (with evidence), reactivity, equilibrium and kinetic control; ~~Burgi-Dunitz trajectory in nucleophilic additions~~; formation of hydrates, cyano hydrins and bisulphite adduct; nucleophilic addition-elimination reactions with alcohols, thiols and nitrogen-based nucleophiles; reactions: benzoin condensation, Cannizzaro and Tischenko reactions, reactions with ylides: Wittig ~~and Corey-Chaykovsky~~ reaction; Rupe rearrangement, oxidations and reductions: ~~Clemmensen~~, Wolff-Kishner, $LiAlH_4$, $NaBH_4$, MPV, ~~Oppenauer, Bouveault-Blanc~~, acyloin condensation; ~~oxidation of alcohols with PDC and PCC; periodic acid and lead tetraacetate oxidation of 1,2-diols.~~

Exploitation of acidity of α-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_2 (Riley) oxidation; condensations (mechanism with evidence): Aldol, Tollens', Knoevenagel, ~~Claisen-Schmidt~~, Claisen ester including Dieckmann, ~~Stobbe;~~ Mannich reaction, Perkin reaction, ~~Favorskii rearrangement~~; a~~lkylation of active methylene compounds~~; ~~preparation and synthetic applications of diethyl malonate and ethyl acetoacetate;~~ specific enol equivalents (lithium enolates, enamines, ~~aza-enolates~~ and silyl enol ethers) in connection with ~~alkylation, acylation and~~ aldol ~~type~~ reaction.

~~*Elementary ideas of Green Chemistry:* Twelve (12) principles of green chemistry; planning of green synthesis; common organic reactions and their counterparts: reactions:~~

~~Aldol, Friedel Crafts, Michael, Knoevenagel, Cannizzaro, benzoin condensation and Dieckmann condensation.~~

Nucleophilic addition to α,β-unsaturated carbonyl system: ~~general principle and mechanism (with evidence)~~; ~~direct and conjugate addition,~~ addition of enolates (Michael reaction), ~~Stetter reaction, Robinson annulation~~.

Substitution at sp^2 carbon (C=O system): mechanism (with evidence): $B_{AC}2$, $A_{AC}2$, $A_{AC}1$, $A_{AL}1$ (in connection to acid and ester); acid derivatives: amides, anhydrides & acyl halides (formation and hydrolysis including comparison).

Organometallics
(5 Lectures) Marks: 08

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 behavior of Grignard reagents; comparison of reactivity among Grignard, organolithiums and organocopper reagents; Reformatsky reaction; ~~Blaise reaction~~; concept of *umpolung* and base-nucleophile dichotomy in case of organometallic reagents.

***CEMACOR07P:* ORGANIC CHEMISTRY-III LAB**
60 (Lectures/Contact Hours) Marks: 25

Experiment -1: Qualitative Analysis of Single Solid Organic Compounds

A. Detection of special elements (N, ~~S~~, Cl, ~~Br~~) by Lassaigne's test

B. Solubility and classification (solvents: H_2O, 5% HCl, 5% NaOH and 5% $NaHCO_3$)

C. Detection of the following functional groups by systematic chemical tests:
aromatic amino ($-NH_2$), aromatic nitro ($-NO_2$), amido ($-CONH_2$, ~~including imide~~), phenolic –OH, carboxylic acid (-COOH), carbonyl (-CHO and >C=O); only one test for each functional group is to be reported.

D. Melting point of the given compound

E. ~~Preparation, purification and melting point determination of a crystalline derivative of the given compound~~
F. ~~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~~) 3** organic compounds.

SEMESTER-V

***CEMACOR12T:* ORGANIC CHEMISTRY-V**

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures Marks: 50

Carbocycles and Heterocycles

(16 Lectures) Marks: 12

Polynuclear hydrocarbons and their derivatives: synthetic methods include Haworth, Bardhan-Sengupta, ~~Bogert-Cook and other useful~~ syntheses (with mechanistic details); ~~fixation of double bonds and Fries rule~~; reactions (with mechanism) of naphthalene, ~~anthracene, phenanthrene~~ and ~~their~~ derivatives.

Heterocyclic compounds: ~~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 synthesis; 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, ~~Madelung and Reissert~~; quinoline: Skraup, ~~Doebner-Miller, Friedlander~~; isoquinoline: Bischler-Napieralski synthesis.

Cyclic Stereochemistry
(10 Lectures) Marks: 08

Alicyclic compounds: concept of I-strain; conformational analysis: cyclohexane, mono and disubstituted cyclohexane; symmetry properties and optical activity; topomerisation; ring-size and ease of cyclisation; conformation & reactivity in cyclohexane system: consideration of steric and stereoelectronic requirements; elimination (E2, E1), nucleophilic substitution (S_N1, S_N2, S_Ni, NGP), merged substitution-elimination; rearrangements; oxidation of cyclohexanol, esterification, saponification, lactonisation, epoxidation, pyrolytic *syn* elimination and fragmentation reactions.

Pericyclic reactions
(8 Lectures) Marks: 08

Mechanism, stereochemistry, regioselectivity in case of
Electrocyclic reactions: FMO approach involving 4π- and 6π-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.

Carbohydrates
(14 Lectures) Marks: 10

Monosaccharides: Aldoses up to 6 carbons; structure of D-glucose & D-fructose (configuration & conformation); ring structure of monosaccharides (furanose and pyranose forms): Haworth representations and non-planar conformations; anomeric effect (including stereoelectronic explanation); mutarotation; epimerization; reactions (mechanisms in relevant cases): Fischer glycosidation, osazone formation, brominewater oxidation, HNO_3 oxidation, selective oxidation of terminal $–CH_2OH$ of aldoses, reduction to alditols, Lobry de Bruyn-van Ekenstein rearrangement; stepping–up (Kiliani-Fischer method) and stepping–down (Ruff's & Wohl's methods) of aldoses; end-group-interchange of aldoses; acetonide (isopropylidene) and benzylidene protections; ring-size determination; Fischer's proof of configuration of (+)-glucose.

Disaccharides: Glycosidic linkages, concept of glycosidic bond formation by glycosyl donor-acceptor; structure of sucrose, inversion of cane sugar.
Polysaccharides: starch (structure and its use as an indicator in titrimetric analysis).

Biomolecules
(12 Lectures) Marks: 12

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 ~~& '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.

CEMACOR12P: ORGANIC CHEMISTRY-V LAB
(60 Lectures/Contact Hours) Marks: 25

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 leaf pigments from spinach leaves~~
4. ~~Column chromatographic separation of mixture of dyes~~
5. Paper chromatographic separation of a mixture containing 2/3 amino acids
6. ~~Paper chromatographic separation of a mixture containing 2/3 sugars~~

B. Spectroscopic Analysis of Organic Compounds

1. Assignment of labelled peaks in the ^{1}H NMR spectra of the known organic compounds explaining the relative δ-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, C≡C, C≡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) *trans*-4-Nitrocinnamaldehyde (xi) Diethyl fumarate (xii) 4-Nitrobenzaldehyde~~ (xiii) 4′-Methylacetanilide (xiv) Mesityl oxide (xv) 2-Hydroxybenzaldehyde (xvi) 4-Nitroaniline ~~(xvii) 2-Hydroxy-3-nitrobenzaldehyde~~ (xviii) 2,3-Dimethylbenzonitrile (xix) Pent-1-yn-3-ol (xx) 3-Nitrobenzaldehyde ~~(xxi) 3-Ethoxy-4-hydroxybenzaldehyde (xxii) 2-Methoxybenzaldehyde (xxiii) Methyl 4-hydroxybenzoate (xxiv) Methyl 3-hydroxybenzoate (xxv) 3-Aminobenzoic acid (xxvi) Ethyl 3-aminobenzoate~~
(xxvii) Ethyl 4-aminobenzoate ~~(xxviii) 3-Nitroanisole (xxix) 5-Methyl-2-nitroanisole (xxx) 3′-Methylacetanilide~~