CHEMISTRY CONCEPT TREE

Organic Chemistry – Some Basic Principles and Techniques

Zeedfolio — NEET Curriculum Master · Class 11 & 12

Concept Tree — Organic Chemistry – Some Basic Principles and Techniques

Depth legend: Chapter · L1 · L2 · L3 · L4 · L5 · L6+ · connectors ★ high-yield ⚠ classic trap

Organic Chemistry – Some Basic Principles and Techniques

- **Tetravalence of Carbon, Shapes and Representation**
  - Hybridisation and Molecular Shape
    - sp^3: 4 σ bonds; tetrahedral; bond angle ~109.5° (CH_4)
    - sp^2: 3 σ + 1 π; trigonal planar; ~120° (C_2H_4, >C=O)
    - sp: 2 σ + 2 π; linear; 180° (C_2H_2, –C≡N)
    - restricted rotation about C=C (sideways p-overlap); π cloud above/below plane = reactive centre
  - s-character Consequences ($sp > sp^2 > sp^3$)
    - more s-character → higher electronegativity of C
    - shorter, stronger bonds; C–H bond enthalpy $sp > sp^2 > sp^3$
    - C–H acidity $sp > sp^2 > sp^3$ (basis of terminal-alkyne acidity)
  - Bond Counting and Unsaturation
    - σ = all single bonds + one per multiple bond
    - π = one extra in C=C, two extra in C≡C
    - degree of unsaturation (IHD) = (2C + 2 + N − H − X)/2
  - Structural Formulae
    - Lewis/dot → dash (complete) → condensed → bond-line
    - bond-line: line junction = C; terminus = CH_3; H added to satisfy tetravalency
  - Three-Dimensional Representation
    - wedge–dash: solid wedge = toward viewer; dashed = away; line = in plane
    - models: framework (bonds only), ball-and-stick, space-filling (van der Waals volume)
- **Classification, Functional Groups and Homologous Series**
  - Classification by Skeleton
    - Acyclic (aliphatic): open straight or branched chain
    - Alicyclic (homocyclic): carbon-only ring, non-aromatic (cyclopropane, cyclohexane)
    - Aromatic
      - benzenoid: benzene, aniline, naphthalene
      - non-benzenoid: tropone
    - Heterocyclic: ring heteroatom
      - alicyclic hetero: tetrahydrofuran
      - aromatic hetero: furan (O), thiophene (S), pyridine (N)
  - Carbon (and Hydrogen) Types
    - 1° C bonded to one other C; 2° to two; 3° to three; 4° to four (no H)
    - 1°/2°/3° hydrogens = H on 1°/2°/3° carbon (feeds halogenation product counting)
  - Functional Group
    - atom/group that governs characteristic chemical properties
    - families: –OH, –CHO, >C=O, –COOH, –COOR, –X, $–NH_2$, –CN, $–NO_2$
  - Homologous Series
    - common general formula; consecutive members differ by $–CH_2$ (14 u)

- gradation in physical, similarity in chemical properties
- two or more groups → polyfunctional compound

IUPAC Nomenclature

- Chain-Selection and Numbering Rules
  - (1) longest continuous chain = parent (must contain principal group)
  - (2) tie → chain with more side chains
  - (3) lowest locant set by "first point of difference"
  - (4) still equivalent → lower number to substituent first alphabetically
  - (5) cite substituents alphabetically
- Substituent Naming Conventions
  - complex substituent in parentheses; its chain numbered from attachment C (=1)
  - di-, tri- multiplying prefixes NOT counted in alphabetising
  - iso-, neo- ARE part of the name (alphabetised)
  - sec-, tert- are NOT counted in alphabetising
- Principal-Group Priority (Seniority, NCERT order)
  - –COOH > –SO_3H > –COOR > –COCl > –$CONH_2$ > –CN
  - > –CHO > >C=O > –OH > –NH_2 > C=C > C≡C
  - highest group = suffix; number so it gets lowest locant
  - –R, –X, –OR, –NO_2 are always prefix substituents
- Common Functional-Group Suffixes
  - alcohol -ol; aldehyde -al; ketone -one; acid -oic acid
  - ester alkyl -oate; amide -amide; nitrile -nitrile; amine -amine
  - mixed example: $HOCH_2CH_2CH_2COCH_3$ = 5-hydroxypentan-2-one (keto senior)
- Cyclic and Benzene Derivatives
  - monocyclic: prefix cyclo-; lowest locant set to substituents
  - benzene: ortho (1,2), meta (1,3), para (1,4) or numeric locants
  - retained trivial parents: toluene, aniline, phenol, benzaldehyde, benzoic acid
- Two-Way Skill
  - structure → name and name → structure (e.g. 1-bromo-5-chloro-4-methylhexan-3-ol)
  - di/tri keeps full parent: ethane-1,2-diol, buta-1,3-diene

Structural (Constitutional) Isomerism

- Chain (Skeleton) Isomerism
  - same formula, different carbon backbone (n-butane vs isobutane)
- Position Isomerism
  - same skeleton, group at different position (propan-1-ol vs propan-2-ol)
- Functional-Group Isomerism
  - same formula, different group (alcohol↔ether; aldehyde↔ketone; acid↔ester)
- Metamerism
  - different alkyl groups either side of a linkage (ethers, ketones, esters, 2° amines)
- Ring-Chain Isomerism
  - cyclic vs open-chain (cyclopropane C_3H_6 vs propene C_3H_6)
- Isomer Counting
  - C_5H_{12} = 3; $C_4H_{10}O$ = 7; enumerate skeletons/positions without double-counting
- Tautomerism
  - rapidly interconverting isomers differing in proton + π-bond position (keto ⇌ enol)
  - keto generally more stable (C=O stronger than C=C)
  - differs from resonance: tautomers differ in connectivity; resonance moves only electrons

- **Stereoisomerism**
  - Geometrical (cis–trans / E–Z)
    - conditions: restricted rotation (C=C or ring) + two different groups on each C
    - E–Z by CIP priority (higher atomic number = higher priority)
    - dipole moment: cis-2-butene > trans; trans-1,2-dichloroethene μ = 0
    - stability: trans generally more stable (less steric strain)
    - ring example: 1,2-dimethylcyclohexane shows cis–trans
  - Optical (Introduction)
    - chirality = non-superimposable on mirror image
    - chiral (asymmetric) carbon = four different groups
    - plane of symmetry → achiral; enantiomers = mirror-image pair
    - racemic mixture = 50:50 enantiomers, net rotation zero
    - max stereoisomers = 2^n (n = chiral centres); meso reduces count (internal symmetry)
    - "including stereoisomers" counting: skeleton × (chiral ×2, C=C cis/trans ×2)
- **Fundamentals of Reaction Mechanism**
  - Fission of Covalent Bonds
    - homolytic: each atom keeps one e^- → free radicals (fish-hook single-barbed arrows)
    - heterolytic: one atom keeps both e^- → carbocation + carbanion (double-barbed arrows)
    - curved arrow: tail at electron source (bond/lone pair) → head at electron sink
  - Attacking Reagents
    - Nucleophiles: electron-rich pair-donors / Lewis bases (OH^-, CN^-, NH_3, H_2O, halides, alkenes)
    - Electrophiles: electron-deficient pair-acceptors / Lewis acids (H^+, NO_2^+, R^+, BF_3, $AlCl_3$)
  - Types of Organic Reactions
    - substitution (→ Haloalkanes: SN1/SN2)
    - addition (→ Hydrocarbons: Markovnikov)
    - elimination (→ Haloalkanes: E1/E2, Saytzeff)
    - rearrangement (carbocation shifts to more stable cation)
- **Electronic Displacement Effects**
  - Inductive Effect (permanent, through-σ)
    - polarisation of σ electrons by electronegativity difference; decays beyond ~3 C
    - +I order: $-O^-$ > $-COO^-$ > $(CH_3)_3C-$ > $(CH_3)_2CH-$ > CH_3CH_2- > CH_3-
    - −I order: $-NR_3^+$ > $-NO_2$ > $-CN$ > $-COOH$ > $-F$ > $-Cl$ > $-Br$ > $-I$ > $-OR$
    - +I stabilises carbocation/radical, destabilises carbanion; −I the reverse
  - Electromeric Effect (temporary, +E / −E)
    - complete transfer of a π-bond electron pair to one atom
    - occurs ONLY in presence of an attacking reagent; reverts when removed
    - when inductive and electromeric oppose, electromeric predominates
  - Resonance / Mesomeric Effect (π and lone-pair delocalisation)
    - Rules for Valid Canonical Structures
      - atoms fixed; only π/lone-pair electrons move
      - same number of paired/unpaired electrons; total charge conserved
      - more stable: more covalent bonds; −ve charge on more electronegative atom
    - +M (electron-donating): $-OH$, $-OR$, $-O^-$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOR$
    - −M (electron-withdrawing): $-NO_2$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-CN$, $-CONH_2$
    - resonance energy = extra stability vs single hypothetical structure
    - bond-length equalisation (both C–O equal in carboxylate ion)
  - Hyperconjugation (Baker–Nathan / no-bond resonance)

- delocalisation of α-C–H σ electrons into empty p orbital or adjacent π bond
- number of hyperconjugating structures = number of α-C–H bonds
- $(CH_3)_3C^+$ has 9 α-C–H → 9 structures → very stable
- stabilises carbocations, free radicals and alkenes (↓ heat of hydrogenation)
- NOT available to carbanions (no electron-deficient centre) — classic trap ⚠

Reactive Intermediates

- Carbocations (carbenium ions)
  - planar, sp^2, electron-deficient (6 valence e^-); from heterolytic C–X cleavage
  - stability 3° > 2° > 1° > methyl (hyperconjugation + inductive)
  - allyl and benzyl resonance-stabilised; Ph_3C^+ very stable
  - vinyl / aryl cations very unstable (sp, no hyperconjugation)
  - destabilised by adjacent –I/–M EWG (–NO_2, –CN, –CF_3)
  - rearranges by 1,2-H / 1,2-alkyl shift to a more stable cation
- Carbanions
  - pyramidal, sp^3; lone pair in sp^3 orbital
  - stabilised by –I/–M EWG (–NO_2, –CN, aryl)
  - stability rises with s-character: $HC{\equiv}C^-$ (sp) > vinyl/aryl (sp^2) > alkyl$^-$ (sp^3)
  - alkyl groups (+I) DESTABILISE (reverse of carbocations)
- Free Radicals
  - sp^2, one unpaired e^-; from homolytic cleavage
  - stability 3° > 2° > 1° > methyl (hyperconjugation, same trend as cations)
  - allyl and benzyl radicals resonance-stabilised

Acidity and Basicity Reasoning

- Acidity Spine (by conjugate-base stability)
  - carboxylic acid > phenol > water > alcohol > terminal alkyne
  - –I EWG raises acidity: FCH_2COOH > $ClCH_2COOH$ > $BrCH_2COOH$ > CH_3COOH
  - +I EDG lowers acidity: HCOOH > CH_3COOH > $(CH_3)_2CHCOOH$ > $(CH_3)_3CCOOH$
  - carboxylate = two equivalent resonance structures (why acid > phenol > alcohol)
- Basicity of Amines
  - aliphatic amine > aromatic amine (aniline: lone pair delocalised into ring, –M)
  - +I of alkyl groups increases basicity
  - aqueous anomaly: 2° > 1° > 3° (balance of +I, steric, solvation of R_3NH^+)

Purification of Organic Compounds

- Sublimation
  - solid → vapour without melting; separates sublimable from non-sublimable impurity
- Crystallisation
  - differential solubility: sparingly soluble cold, appreciably soluble hot
  - impurities stay in mother liquor; coloured impurity removed by decolourising charcoal
  - repeated crystallisation for impurities of comparable solubility
- Distillation Family
  - Simple: volatile from non-volatile / large bp gap ($CHCl_3$ b.p. 334 K + aniline b.p. 457 K)
  - Fractional: small bp gap; fractionating column = many theoretical plates; crude-oil refining
  - Reduced-pressure: high-boiling / thermolabile; glycerol from spent-lye in soap industry
  - Steam: steam-volatile + water-immiscible; boils when $p_1 + p_2$ = atmospheric (below own bp); aniline
- Differential Extraction
  - shake aqueous solution with immiscible organic solvent in separating funnel; distil off solvent
  - continuous extraction when compound is only slightly solvent-soluble

- Chromatography
  - Adsorption (differential adsorption on silica/alumina)
    - Column: mixture on top of packed column; eluant flows down; most-adsorbed retained near top
    - TLC: thin adsorbent layer on plate; Rf = dist. by substance / dist. by solvent front
  - Partition (differential partition between two phases)
    - Paper chromatography: water on cellulose = stationary; solvent = mobile phase
  - Visualisation: UV light, iodine vapour, ninhydrin spray (amino acids)

Elemental Analysis

- Qualitative Detection
  - Carbon and Hydrogen (heat with CuO)
    - C → CO_2 → limewater [$Ca(OH)_2$] turns milky
    - H → H_2O → anhydrous $CuSO_4$ turns blue
  - Lassaigne's (Sodium Fusion) Test — covalent → ionic (fuse with Na)
    - Nitrogen: Na + C + N → NaCN; + $FeSO_4$ → $Na_4[Fe(CN)_6]$; + Fe^{3+} → $Fe_4[Fe(CN)_6]_3$ (Prussian blue)
    - Sulphur: Na + S → Na_2S; + lead acetate → black PbS; + sodium nitroprusside → violet $Na_4[Fe(CN)_5NOS]$
    - N and S together: NaSCN → blood-red $[Fe(SCN)]^{2+}$ (no Prussian blue); excess Na → NaCN + Na_2S
    - Halogens: Na + X → NaX; acidify (HNO_3) + $AgNO_3$ → AgX
      - AgCl white, soluble in NH_4OH
      - AgBr pale yellow, sparingly soluble in NH_4OH
      - AgI yellow, insoluble in NH_4OH
      - if N/S present: boil extract with conc. HNO_3 first (destroy CN^-/S^{2-} interference)
    - Phosphorus: oxidise (Na_2O_2) → phosphate; + ammonium molybdate/HNO_3 → yellow ppt
- Quantitative Estimation
  - Carbon and Hydrogen (combustion over CuO/O_2)
    - % C = (12/44) × (mass CO_2 / mass sample) × 100
    - % H = (2/18) × (mass H_2O / mass sample) × 100
  - Nitrogen — Dumas Method
    - heat with CuO in CO_2 atmosphere → N_2 collected over KOH (aqueous)
    - % N = (28 / 22400) × (V_{N_2} at STP in mL / mass sample) × 100
    - applicable to ALL nitrogen compounds
  - Nitrogen — Kjeldahl's Method
    - digest with conc. H_2SO_4 → $(NH_4)_2SO_4$; + NaOH → NH_3 distilled into standard acid; back-titrate
    - % N = 1.4 × M_{acid} × V_{acid} (mL) / mass sample (g)
    - NOT valid for nitro, nitroso, azo and ring (pyridine) nitrogen
  - Halogens and Sulphur — Carius Method
    - heat with fuming HNO_3 (+ $AgNO_3$) in sealed Carius tube
    - halogen → AgX: % X = (at. mass X / molar mass AgX) × (mass AgX / mass sample) × 100
    - sulphur → $BaSO_4$: % S = (32/233) × (mass $BaSO_4$ / mass sample) × 100
  - Oxygen — by difference
    - % O = 100 − (% C + % H + % N + % S + % halogen)
  - Empirical and Molecular Formula
    - % ÷ atomic mass → mole ratio → ÷ smallest → empirical formula
    - molecular formula = n × empirical; n = molecular mass / empirical formula mass