Core Concepts for Organic Literature Exams:

- Valency, Lewis structures, geometry of atoms
- Molecular orbital theory including – bsics of frontier molecular orbital (FMO) theory (HOMO & LUMO)
- Hybridization: how it affects bond lengths, reactivity….
- Resonance: contributors and hybrids, relative energy of contributors and effect on structure
- Functional groups – their properties
- Electronegativity, inoization potential, electron affinity and inductive effects (electron-withdrawing, electron-donating groups)
- Hydrogen-bonding – which atoms can engage in this? Under what conditions?
- Conformations of alkanes– dihedral angles, anti, gauche, eclipsed, etc.
- Conformations of substituted cyclohexanes – chair, boat, ring flipping, axial vs equatorial
- Aromaticity and antiaromaticity
- Stereochemistry,
  i) Chirality, enantiomers, R/S, D/L configurations, diastereomers, racemic, meso compounds (symmetry elements, mirror planes, inversion center and relationship to both)
  ii) Fisher structures, Newman projections, sawhorse structures
  iii) Stereoselectivity, stereospecificity
- Reactivity: electrophile vs. nucleophile
- Reactive intermediates – their properties, effect of structure on stability, and reactivity
- Solvents and solvent effects- polar, apolar, coordinating, noncoordinating, polarizable, etc.
- Acid-base reactions:
  i) Bronsted-Lowry vs. Lewis
  ii) Role of pKa: pka of func. groups, effect of structure, predicting equilibrium constants
  iii) Basics of hard-soft acid base (HSAB) theory and application to reactivity
- Kinetics: transition state theory; transition states and reaction intermediates; reaction coordinates; catalysis; rate-laws; steady-state approximation
- Equilibrium and connection of equilibrium constants to free energy differences
- Tautomerism – including keto-enol tautomerism
- Reaction coordinate diagrams
  i) Enthalpy: Endothermic and exothermic
  ii) Hammond postulate- early & late transition states, and implications
  iii) Kinetic vs. thermodynamic control; kinetic vs. thermodynamic product
- Gibbs free energy – endergonic, exergonic
-Entropy
- Nucleophilic substitutions
  i) SN1 versus SN2
  ii) Effect of structure on mode of reaction, kinetics, stereochemical outcomes
- Elimination reactions – E1 versus E2; Zaitzev versus anti-Zaitsev
- Competing SN and E reactions
- Addition reactions
  i) Electrophilic addition to olefins (Hal2, Hal2 + H2O, carbenes)
  ii) Syn additions to olefins (hydrogenolysis, hydroboration, etc)
  iii) Regioselectivity- Markovnikov and anti-Markovnikov mechanisms
- Enolate chemistry: Aldol reaction (addition), aldol condensation (addition-elimination), Robinson annulation, Knoevenagel condensation, etc.
- Free radical substitution, addition, polymerization; initiation of radical chain reactions
- Diels-Alder and other pericyclic reactions
- Oxidations and reductions (ozonolysis, hydrogenation, oxidative cleavage,

dihydroxylation, epoxidation)
- Rearrangements and migrations
- Carbonyl addition and addition-elimination reactions
  i) Hydrates, hemiacetals, acetals, imines, enamines, etc.
  ii) Wittig reaction and its variations
  iii) Grignard and other organometallics
- Acyl substitutions – functional group transformations, relative reactivity of acid derivatives
- Electrophilic aromatic substitution – Friedel-Crafts, halogenation, nitration, sulfonation; directing groups, activating and deactivating groups
- Nucleophilic aromatic substitution:
  i) Addition-Elimination via Meissenheimer complex
  ii) elimination-addition via benzyne
- Organometallic chemistry- 18-electron rule; electron counting identification of oxidation states; basics of bonding in organometallic complexes, fundamental organometallic reactions- oxidative addition, reductive elimination, migratory insertions, beta-hyrdide elimination, transmetallation etc.; Metal catalyzed carbon bond forming reactions- Stille, Suzuki, Heck, etc.,