Important Review Topics from Organic Chemistry 1

- Concepts related to stereochemistry and general organic structures.
- Acid-Base Chemistry
- Reaction Energetics
- Some important reactions will be of use in multi-step syntheses:
  - Substitution and Elimination (S_N1, S_N2, E1, E2)
  - H-C≡C: ions as nucleophiles
  - Addition reactions to double and triple bonds
  - Hydrogenation Reactions

Primary Topics from Organic Chemistry 2

Chapter 11
- Reactions of Alcohols & Ethers (review from first semester)
- Epoxides
  - Reactions and Mechanisms

Chapter 12
- General Concepts: Oxidation / Reduction Reactions and Carbonyls
- Oxidations:
  - \( \text{H}_2\text{CrO}_4 \) & Jones Reagent
  - PCC
- Hydride Reductions:
  - \( \text{NaBH}_4 \)
  - \( \text{LiAlH}_4 \)
  - DIBAL-H (Ch.16)
  - tri-tert-butoxyaluminum hydride (Ch.16)
- Organometallic Reactions
  - Grignard Reactions
  - Alkyl Lithium Reagents

Chapter 13
- Conjugated, \( \pi \) systems
  - Electron delocalization
  - Resonance Stabilization
  - Molecular Orbital Theory
  - UV / Vis Spectroscopy
- Allylic groups
- Allyl Radical and Allyl Cation
  - Reactions and Mechanisms
- Polyunsaturated Hydrocarbons
  - 1,4 additions
- Diels-Alder Reaction

Note on molecular orbitals and conjugated \( \pi \) systems
- Be familiar with the HOMO & LUMO, as well as \( \pi \) bonding, non-bonding, and \( \pi^* \) antibonding orbitals.
- Understand their importance in UV/Vis spectroscopy as well as chemical reactions (allyl radical and cation).
Chapter 14
- Aromatic Compounds
- Predicting aromaticity
  - 4n+2 rule
  - Cyclical, planar, conjugated \( \pi \) system
- Molecular Orbitals
  - Relative energies

Chapter 15
**Electrophilic Aromatic Substitution**
- EAS – General Mechanism
- EAS Reactions:
  - Halogenation
  - Nitration
  - Sulfonation
  - Friedel-Crafts alkylation
  - Friedel-Crafts acylation
- Ortho-para directors
  - Activating (resonance stabilization)
  - Deactivating (halides)
- Meta directors
  - Deactivating (partial positive charge adjacent to the ring)

**Carbonyl Compounds (Multiple Chapters)**
- Properties
- Classes of carbonyl compounds

Chapter 16
- Aldehydes and Ketones
  - General properties and reactivity
- Hemiacetals and Acetals
  - Structure
  - Acid-catalyzed formation
  - Base-catalyzed formation
  - Role of acetals as protecting groups (consider ethylene glycol)
- Wittig Reaction
- Imenes & Enamines

Chapter 18
- Carboxylic Acids & Derivatives
  - Basic structure, nomenclature, and reactivities of:
    - Carboxylic acids
    - Carboxylate anions
    - Esters
    - Amides
    - Acid Chlorides
    - Anhydrides
- Esterification
  - Acid-catalyzed esterification & hydrolysis
  - Saponification (base-promoted hydrolysis)
  - Trans-esterification
Chapter 18 (cont.)

- Acid Chlorides
  - Synthesis from carboxylic acids – SOCl₂, PCl₃, PCl₅
  - Conversions to other carboxylate derivatives – conditions and mechanism
- Anhydrides
  - Synthesis from acid chlorides and carboxylic acids.
  - Cyclic anhydrides
  - Conversions to esters and amides
- Amides
  - Synthesis from acid chlorides & anhydrides.
  - Hydrolysis (acidic or basic conditions)
  - Amine protecting groups.
- Nitriles
  - Cyanide ion as a nucleophile
  - Acidic or basic hydrolysis of a nitrile
  - Grignard Reduction of a nitrile (section 16.5D)

Chapter 17 & Chapter 19

- Enols & Enolates
  - Acidity of the α hydrogen
  - Resonance-stabilization of the enolate ion
- Keto-enol tautomerization
  - Acid & Base catalysis
  - Racemization of chiral ketones
- Aldol Reaction
  - Reaction Process of an aldol condensation:
    - Aldol Addition
    - Dehydration of the Aldol addition product (formation of the α,β unsaturated carbonyl)
- Mechanisms for Aldol formation / dehydration reactions with acid or base catalysis
- Aldehyde vs. Ketone reactivity
- Reversibility
- Crossed Aldol Reactions
- Claisen-Schmidt Reactions
- Intramolecular Aldol Condensations (ring formation)
- Lithium Enolates (17.7)
  - LDA – Lithium diisopropyl amide as a strong base
  - Regioselectivity of enolate reactions
  - Thermodynamic enolate vs. Kinetic enolate
  - Aldol & Claisen-Schmidt reactions with lithium enolates
  - Direct Alkylation of ketones
- Addition to α,β-unsaturated aldehydes & ketones (17.9)
  - Simple addition at the carbonyl carbon vs. conjugate addition at the β carbon.
    - Reactivity of the nucleophile.
  - Michael Addition
    - Conjugate addition of an enolate.
  - Robinson Annulation
    - Michael addition, followed by an aldol reaction to produce a ring.
Chapter 17-19 (cont.)

- β-dicarbonyl compounds (19.1 – 19.2A)
  - Acidity
  - Claisen Condensation
    - Formation of a β-keto ester
  - Dieckmann Condensation (Intramolecular Claisen)
  - Crossed Claisen
  - Hydrolysis of a β-keto ester (acidic or basic conditions) to a β-keto acid
  - Decarboxylation of a β-keto acid (section 18.10)