Test 4 Topic Summary – Chapters 23-25

Chapter 23: Carbonyl Condensation Reactions

- Aldol Condensation - ketone/aldehyde as nucleophile and electrophile – **mechanism**
- Aldol condensation vs. α–Substitution (base strengths: LDA vs. $^{-}$OH)
- Dehydration (elimination) of aldol product to form α,β–unsaturated ketone/aldehyde – **mechanism**
- Mixed Aldol – when do we get only one product? – **mechanism**
- Intramolecular Aldol – cyclization reaction – **mechanism**
- Claisen Condensation – Aldol type reaction with esters – **mechanism**
- Mixed Claisen – when do we get only one product? – **mechanism**
- Dieckman Cyclization (Intramolecular Claisen) – **mechanism**
- Michael Addition - enolate attacks α,β–unsaturated carbonyl compound (1,4-addition) – **mechanism**
  - Good Michael Donors: stable enolates (eg diethyl malonate)
  - Good Michael Acceptors: α,β–unsaturated aldehydes, ketones, esters, nitriles, amides, nitro compounds
- Robinson Annulation - Michael Addition followed by Aldol Condensation

Chapter 24: Amines

- Naming
- Basiscity of amines - fine tuning with electron withdrawing/donating groups
- Synthesis of amines
  - Azide synthesis **- mechanism**
  - Gabriel synthesis - **mechanism**
  - Reduction of amides
  - Reduction of nitriles
  - Reductive amination - **(imine formation ch. 19)**
  - Hoffman Rearrangement of amide – **mechanism**
  - Curtius Rearrangement of acyl azide – **mechanism**
- Reactions of amines
  - Amides from amine and acid chloride
  - Hoffman Elimination (makes non-Saytsev alkene)
- Basicity of arylamines, including "tuning"
- Synthesis of arylamines
  - From aromatic nitro compounds
- Reactions of arylamines
  - Normal Electrophilic Aromatic Substitution reactions (very reactive) (ch.16)
  - Conversion to amide to avoid polyadditions

Chapter 25: Carbohydrates

- Classification - aldose vs. ketose, tri, tetra, etc.
- D,L sugars
- Know names and structures for D-aldotriose through D-aldohexoses (15 sugars)
- Hemiacetal formation - pyranose, furanose forms - alpha (trans) and beta (cis) forms – **mechanism (chapter 19)**
- Chair conformations and Haworth Projections

–over–

- Ester formation
- Ether formation
- Glycoside formation (acetal)
- Reduction to alditol
- Oxidation to aldonic acids
- Oxidation to aldaric acids
- Kiliani-Fischer chain lengthening
- Wohl Degradation
- Disaccharide linkages (usually 1, 4')