Review Sheet – CH 254, Exam #3

The exam will cover Chapters 16 and 17, and parts of 18.

Chapter 16 Topics
- Conversion of carboxylic acids to acid chlorides (know mechanism)
- Reactions of acid chlorides, anhydrides, esters, amides. [This is generic acyl substitution, including acid and base catalyzed hydrolysis. Know the mechanisms.]
- Specifics:
  - Fischer esterification (know mechanism in both directions)
  - Hydrolysis of nitriles (know mechanism)
- **SKIP: 16.18 (Gabriel Synthesis) and 16.22**

Chapter 17 Topics
- Nomenclature of aldehydes and ketones
- Relative reactivities of all carbonyl compounds (Chapters 16 & 17)
- Various redox reactions (see tables in your notes)
- Also simple oxidations of aldehydes (Ag₂O and the Tollens test – Ag(NH₃)₃⁺)
- Baeyer-Villiger Oxidation (aldehydes → carboxylic acids; ketones → esters)
- Grignard reaction (revisited)
  - RMgX + formaldehyde → 1° alcohol
  - RMgX + aldehyde → 2° alcohol
  - RMgX + ketone → 3° alcohol
  - RMgX + ester → 3° alcohol (two identical R’s)
  - RMgX + CO₂ → carboxylic acid
  - RMgX + nitrile → ketone
- Acid chloride + LiCuR₂ → ketone
- Carbonyls + oxygen nucleophiles (hydrates, hemiacetals, acetals). Know mechanisms in both directions. Be able to use protecting groups appropriately.
- Carbonyls + sulfur nucleophiles → thioacetals (use Ra-Ni to reductively cleave C-S bond)
- Carbonyls + nitrogen nucleophiles
  - Ammonia/primary amines → imines
  - Secondary amines → enamines
  - Tertiary amines → NRX
  - Hydroxylamine (NH₂OH) → oxime (C=N-OH)
  - 2,4-DNP or other hydrazines → hydrazones (C=N-NHZ)
  - Wolff-Kishner reduction – know the mechanism
- Carbonyls + phosphorus nucleophiles – this is the Wittig reaction. Know the mechanism.
- Carbonyls + acetylide anions → propargyl alcohols
- Carbonyls + NaCN/HCN → cyanohydrins
- **SKIP: Reductive Amination (p. 812); 17.14; 17.17-17.18**
Chapter 18 Topics

- **SKIP: 18.6**
- Enolization racemizes the alpha carbon.
- Know mechanism for enol/enolate formation in acid/base.
- Halogenation in acid (stops after one addition)
- Halogenation in base (continues until you run out of alpha protons) – haloform reaction
- Decarboxylation of β-keto acids with heat
- Hell-Volhard- Zelinsky reaction (α-bromination of carboxylic acids)