

# Review Sheet – CH 254, Exam #3

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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 ( $\text{Ag}_2\text{O}$  and the Tollens test –  $\text{Ag}(\text{NH}_3)_3^+$ )
- Baeyer-Villiger Oxidation (aldehydes  $\rightarrow$  carboxylic acids; ketones  $\rightarrow$  esters)
- Grignard reaction (revisited)
  - $\text{RMgX} + \text{formaldehyde} \rightarrow 1^\circ \text{ alcohol}$
  - $\text{RMgX} + \text{aldehyde} \rightarrow 2^\circ \text{ alcohol}$
  - $\text{RMgX} + \text{ketone} \rightarrow 3^\circ \text{ alcohol}$
  - $\text{RMgX} + \text{ester} \rightarrow 3^\circ \text{ alcohol}$  (two identical R's)
  - $\text{RMgX} + \text{CO}_2 \rightarrow \text{carboxylic acid}$
  - $\text{RMgX} + \text{nitrile} \rightarrow \text{ketone}$
- Acid chloride +  $\text{LiCuR}_2 \rightarrow \text{ketone}$
- Carbonyls + oxygen nucleophiles (hydrates, hemiacetals, acetals). Know mechanisms in both directions. Be able to use protecting groups appropriately.
- Carbonyls + sulfur nucleophiles  $\rightarrow$  thioacetals (use  $\text{Ra-Ni}$  to reductively cleave C-S bond)
- Carbonyls + nitrogen nucleophiles
  - Ammonia/primary amines  $\rightarrow$  imines
  - Secondary amines  $\rightarrow$  enamines
  - Tertiary amines  $\rightarrow$  NRX
  - Hydroxylamine ( $\text{NH}_2\text{OH}$ )  $\rightarrow$  oxime ( $\text{C}=\text{N-OH}$ )
  - 2,4-DNP or other hydrazines  $\rightarrow$  hydrazones ( $\text{C}=\text{N-NHZ}$ )
  - Wolff-Kishner reduction – know the mechanism
- Carbonyls + phosphorus nucleophiles – this is the Wittig reaction. Know the mechanism.
- Carbonyls + acetylide anions  $\rightarrow$  propargyl alcohols
- Carbonyls +  $\text{NaCN}/\text{HCN} \rightarrow$  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  $\beta$ -keto acids with heat
- Hell-Volhard- Zelinsky reaction ( $\alpha$ -bromination of carboxylic acids)