

Review Sheet – CH 254, Exam #4

The exam will cover the rest of Chapter 18, all of Chapter 19, and all of Chapter 20.

Chapter 18 Topics

- ❖ Aldol reaction (includes crossed aldol and cyclizations) (*know mechanism*)
- ❖ Stork enamine synthesis
- ❖ Alkylation at the alpha position (lithium enolates)
- ❖ Simple & conjugate addition (*know mechanism*)
- ❖ Michael addition
- ❖ Claisen & Dieckmann condensation
- ❖ Decarboxylation of alpha-keto acids
- ❖ Acetoacetic ester synthesis
- ❖ Malonic ester synthesis

Chapter 19 Topics

- ❖ Catalytic hydrogenation (various catalysts)
- ❖ “Dissolving” metal reductions – includes the Birch reduction
- ❖ Hydride reductions – NaBH_4 , LiAlH_4 , DIBAL, $\text{LiAlH}(\text{OtBu})_3$
- ❖ Chromic acid oxidation
- ❖ PCC
- ❖ Swern oxidation (DMSO, oxalyl chloride, Et_3N)
- ❖ Oxidation of aldehydes and ketones – includes the Baeyer-Villiger oxidation and the haloform reaction.
- ❖ Hydroxylation of alkenes
- ❖ Oxidative cleavages
 - Of vicinal diols

- Ozonolysis of alkenes
- Permanganate cleavage of alkenes
- Of alkynes

Chapter 20 Topics

- ❖ Nomenclature (including heterocycles)
- ❖ Structure/bonding/relative basicities (in solution: amides < arylamines < ammonia < 1° < 3° < 2°)
- ❖ Synthesis
 - alkylation of ammonia (S_N2) → 1° amine only
 - Gabriel synthesis (S_N2) → 1° amine only
 - reductions
 - RX + NaN₃ (S_N2) followed by LiAlH₄ reduction → 1° amine only
 - reduce nitriles and oximes with LiAlH₄ → CH₂NH₂ only
 - reduce nitro groups with Fe⁰/HCl then NaOH → 1° amine only
 - reductive amination (via the imine) - aldehyde/ketone + ammonia/1°/2° amine + H₂/Ni or NaCNBH₃ or NaBH(OAc)₃ → 1°/2°/3° amines (always CH-NH)
 - reduce amides with LiAlH₄ → 1°/2°/3° amines (always CH₂N)
 - Hofmann Rearrangement (1° amides only → 1° amines) (*know mechanism*)
- ❖ Reactions
 - react with aldehydes/ketones → imines and enamines
 - react with acyl chlorides → amides
 - exhaustive methylation (CH₃I)
 - Hofmann Elimination
 - oxidation of 3° amines → 3° amine oxides
 - Cope Elimination
- ❖ Aromatic heterocycles
 - Know EAS mechanism; which position tends to react