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, $LiAlH(O\mathit{t}Bu)_3$
- 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 + NaN_3 (S_N2) followed by $LiAlH_4$ reduction → 1° amine only
    - reduce nitriles and oximes with $LiAlH_4$ → CH_2NH_2 only
    - reduce nitro groups with Fe°/HCl then NaOH → 1° amine only
    - reductive amination (via the imine) - aldehyde/ketone + ammonia/1°/2° amine + H_2/Ni or $NaCNBH_3$ or $NaBH(OAc)_3$ → 1°/2°/3° amines (always CH-NH)
    - reduce amides with $LiAlH_4$ → 1°/2°/3° amines (always CH_2N)
  - Hofmann Rearrangement (1° amides only → 1° amines) *(know mechanism)*
- Reactions
  - react with aldehydes/ketones → imines and enamines
  - react with acyl chlorides → amides
  - exhaustive methylation (CH_3I)
  - Hofmann Elimination
  - oxidation of 3° amines → 3° amine oxides
  - Cope Elimination
- Aromatic heterocycles
  - Know EAS mechanism; which position tends to react