CHEM 8B, Lecture 1
- Mini-8A Overview
- CH 16.1-16.3 – Electrophilic Aromatic Substitution (EArS)
  - Halides
  - Heteroatoms
  - Carbons (Alkylation & Acylation)

Functional Groups
= Organizing ochem by specific bonding patterns
- Be able to identify & draw a simple example of each from Table 3.1 including…

Skill Check: Arrow Pushing
** Arrows start at Electron Rich (Nucleophile) and end at Electron Poor (Electrophile)**
Add arrows with a note – which bonds are broken and/or formed according to that arrow?

Reflect on mistakes: did you have different arrows? Copy your mistakes below and/or your neighbor’s mistakes. Discuss what those incorrect arrows mean and why it’s incorrect.
Acid-Base Chemistry

\[ \text{B: H} \rightleftharpoons \text{A} \]

pKa’s to memorize in Study Expectations & Learning Advice (also in 8B Lecture 3)

Add those standards and pKa’s here on your own time:

Direction of equilibrium: Who wants that proton (H⁺) more??

Compare acid (left) to conjugate acid (right)…weaker acid (lower pKa) favored

\[ \text{CH}_3\text{OH} \quad \text{CH}_3\text{NH}_2 \]

Reaction Mechanisms

Any mechanisms from 8A that you need to know will be reviewed in 8B, starting with...

Chapter 8 – Electrophilic Addition to Alkenes

\[ \text{H-Br} \quad \text{[ ]} \]

Chapter 11 – E1 = unimolecular elimination

\[ \text{LG} \quad \text{[ ]} \quad \text{ex. CH}_3\text{OH} \]
CHAPTER 16, PART 1 \( \rightarrow \) **Electrophilic Aromatic Substitution (EArS)** of Benzene

*Template EArS Mechanism*

\[
\text{Cl}_2 + \text{FeCl}_3 \rightarrow \quad \text{Cl}^+ + \text{Base}
\]

\[
\text{Br}_2 + \text{FeBr}_3 \rightarrow
\]

\[
\text{I}_2 + \text{CuCl}_2 \rightarrow
\]

**Representative chlorination mechanism**

\[
\text{HNO}_3 + \text{H}_2\text{SO}_4 \quad \rightarrow \quad \text{H}_2\text{SO}_4
\]

**Heteroatoms (N & S)**

**Nitration**

**Sulfonation**
Friedel-Crafts (FC) Reactions (Rxns) ***Add C’s to Benzene***

**FC Acylation**
- No C⁺ RRGTs

**FC Alkylation**
- Start Simple…

- Is there a more substituted carbon on the alkyl halide?

Alkyl C⁺ rearranges to more substituted C
Hydride Shifts in FC Alkylations

How to handle this…
1. Don’t panic!
2. Start the mechanism as usual
3. Draw C leading to major product (work backwards)

Alkyl Shifts in FC Alkylations
…when a hydride shift is not an option (quaternary C nearby)

Reaction Puzzle – fill in the boxes and add missing reagents over blank arrows
Memory Retrieval – write down as many reactions as you can in the time given, without looking at notes or other resources. This could include any new reactions from today and any 8A reactions. Note to future self: do not wait to review / relearn 8A reactions if it's been a while since you took that class!

Next time… Synthesis of Disubstituted Benzene: Substituent Effects
- 16.4-16.5 – use the reading questions to make efficient use of reading time (~30 min)
- Electron withdrawing groups (EWG) vs. electron donating groups (EDG)
- Ortho/para vs. meta-directors
- Activators and deactivators for another EArS reaction