

Advice for 8A Review – McMurry Chapter 1-11,14,15 – Start this ASAP!

- *A good way to start:* work through the 8A worksheets & exams online
- *Fundamental Topics:* functional groups, resonance, arrow-pushing, nomenclature, stereochemistry (assigning R/S), & acid-base chemistry, memorizing the approximate pKa's for the following standards...
 - HCl (-7), hydronium H_3O^+ (0), acetic acid $\text{CH}_3\text{CO}_2\text{H}$ (5), H_2S (7), phenols PhOH (10), ammonium NH_4^+ (10), water H_2O (16), acetone CH_3COCH_3 (19), ammonia NH_3 (35), and methane CH_4 (50)
- *Nucleophiles & Electrophiles* – by far the most important fundamental concept. As you review the reactions from 108A, make a list of nucleophiles & electrophiles (organize by functional group). Keep this as a running tally as you learn new reactions in 108B.
- Know the reactions from Chapters 7-11 & 14 (alkenes, alkynes, organohalides, $\text{S}_\text{N}1/\text{S}_\text{N}2/\text{E}1/\text{E}2$, and conjugated compounds) – these reactions will come up again in lecture & HW. It will be obvious which reactions you need to know by the first exam.

Preparing for Lecture: This document is designed to help guide your reading by providing the *bare minimum* material you should be familiar with when you walk into lecture. Begin your reading assignment by finding the responses to the questions or statements that follow. *The responses are not turned in for credit but may show up on quizzes in discussion.* Complete the reading by skimming the text, becoming familiar with bold terms, and making some sense of the figures, schemes, tables etc. You are not expected to fully understand everything before lecture, but familiarity makes a big difference in your ability to follow lectures. Time permitting, you may decide to look up an individual topic on the [Khan Academy Website for OChem](#).

Lecture 1, Chapter 16.1-16.3

1. Draw the mechanism for electrophilic addition to alkenes (reaction with HCl).
2. Draw the mechanism for electrophilic aromatic substitution and compare to #1.
3. Identify the nucleophile and electrophile in the first step of the following reactions. Typically the electrophilic species is formed over several steps before actual reaction with benzene.
 - Bromination, chlorination, and iodination of benzene (3 separate reactions)
 - Nitration and sulfonation of benzene (2 rxns)
 - Friedel-Crafts alkylation and acylation reactions (2 rxns)

Lecture 2, Chapter 16.4-16.5

1. Know which groups classify as *meta*-directing deactivators, *ortho*- and *para*-directing deactivators, and *ortho*- and *para*-directing activators.
2. Draw the main contributing resonance structures of the following compounds: phenol, aniline, acetophenone, nitrobenzene, and fluorobenzene. How does the charge on the rings reflect whether the group is donating or withdrawing?

Lecture 3, Chapter 16.6, 16.9-16.11

1. Review the direction of substitution with di-substituted benzenes.
2. Be able to identify the “benzylic” position and why this position can be reactive.
3. What atoms are broken/formed in oxidation reactions? In reduction reactions?

Chapter 17.1-17.3

1. Be able to draw a compound from the name, where it contains an alcohol or phenol and an alkene or benzene ring.
2. Under what circumstances do alcohols/phenols act like nucleophiles? Like electrophiles?
3. What is an alkoxide? A phenoxide?
4. List the reactions learned in 8A for the synthesis of alcohols.

Lecture 4, Chapter 17.4-17.7

Prepare for pKa game using lecture handout – color & cut (arts & crafts!)

1. Do carbonyl compounds tend to act like nucleophiles or electrophiles?
2. Do Grignard reagents behave as nucleophiles or electrophiles? Are they acidic or basic?
3. Aside from Bronsted-Lowry acid-base reactions, do alcohols tend to act as nucleophiles or electrophiles?
4. Under what conditions can an –OH be turned into a leaving group?
5. What functional groups can a primary alcohol be oxidized into? A secondary alcohol?
6. Why don't tertiary alcohols react with most oxidizing agents?

You do not need to know the mechanisms for the oxidation of alcohols.

Lecture 5, Chapter 18.1-18.3, 18.5-18.6

1. Be familiar with drawing an ether from its name.
2. What reactions from 8A produced ethers?
3. What are the two complementary methods for ether synthesis described in section 18.2?
4. Ethers tend to be used as inert organic solvents. Under what conditions do they react?
5. What is an epoxide?
6. What reaction(s) from 8A produced epoxides?
7. Why are epoxides more reactive than other ethers? How does an epoxide react differently under acidic vs. basic conditions?

Lecture 6, p. 712-716 and Chapter 19.1-19.7

1. Be familiar with drawing structures of aldehydes and ketones from a name.
2. Review alcohol oxidations (Ch 17) to make a list of the different ways to make aldehydes, ketones, and carboxylic acids.
3. In the reactions of aldehydes and ketones, is the carbonyl C a nucleophile or electrophile? Draw the mechanism for nucleophilic addition to aldehydes/ketones with a generic nucleophile "Nu" (p. 729).
4. Draw four separate mechanisms for the nucleophilic addition of water (basic conditions, OH^-), HCN, sodium borohydride (NaBH_4), and methyl magnesium bromide (CH_3MgBr), and to acetone. These mechanisms can be found on p. 732-735! *These mechanisms won't be covered on the first exam but are fair game for exam 2 and the final.*

Lecture 7, p. 717-720 and Chapter 19.8-19.11

1. List all the different nucleophiles that will react with an aldehyde or ketone (including Lecture 7 reactions). Specifically which atom is the electrophile? The nucleophile?
2. What's the difference between an amine, amide, imine, and enamine?
3. Draw the mechanism for the addition of methylamine to acetone. Do the same for dimethylamine and acetone.
4. How does the Wolff-Kishner reduction differ from the reduction of aldehydes and ketones with hydride reagents? You do not need to know the Wolff-Kishner mechanism.
5. What kind of bond is formed in the Wittig reaction? You do not need to know the Wittig mechanism.
6. What is an acetal? Draw the mechanisms for the acid-catalyzed addition of methanol to acetone. Copy the mechanism from p. 744 at least twice. You'll be glad you did!

Lecture 8, Chapter 20.1-20.7

1. Be familiar with drawing structures from names containing carboxylic acids, nitriles, alkenes, and/or alcohols.
2. Which substituents make carboxylic acids more acidic? Less acidic?
3. Review reactions learned earlier in this quarter for synthesizing carboxylic acids.
4. Do nitriles tend to act as nucleophiles or electrophiles?

Lecture 9, Chapter 21.1-21.4, 21.6-21.7

1. Be familiar with drawing structures of carboxylic acid derivatives from their name: acid halides, acid anhydrides, esters, amides, thioesters, and acyl phosphates. Suffixes will be provided on exams.
2. Draw the template mechanism for Nucleophilic Acyl Substitution (NAS).
3. List the carboxylic acid derivatives in order to reactivity towards NAS.
4. List the different carboxylic acid derivatives and figure out how to turn one into any other – especially acid halides, esters, and amides. Which reactions require a catalyst?

Lecture 10, Chapter 22.1-22.6

1. Draw the keto and enol forms of cyclohexanone and acetone.
2. Rationalize the relative acidities of the carbonyl compounds from Table 22.1.
3. What electrophiles will react with enolate ions?
4. How does the alpha-bromination of aldehydes and ketones under basic vs. acidic conditions differ?
5. What drastic change is made if a methyl ketone undergoes bromination under basic conditions?
6. How does the alpha-bromination of aldehydes and ketones vs. carboxylic acids differ?

Lecture 11, Chapter 23.1-23.3

1. Draw the mechanism and product of a simple aldol reaction (acetaldehyde with NaOH).
2. Review the mechanism for dehydration.

Lecture 12, Chapter 24.1-24.8

Reactions skipped in this chapter: Hoffman elimination, Hoffman & Curtius rearrangements

1. Be familiar with drawing structures of amines, ammonium compounds, and N-containing benzene derivatives from their name.
3. Rationalize the acidity/basicity of the amines in Tables 24.1 and 24.2.
4. Be familiar with the Henderson-Hasselbach equation.
5. Before you read section 24.6 (synthesis of amines), recall as many reactions for the synthesis of amines that you've already learned. There should be a lot!
6. What are the main two steps in reductive amination?
7. Review Electrophilic Aromatic Substitution (EArS, from Ch 16). Be familiar with how this applies to arylamines.
8. What is a diazonium salt? How do these compounds behave in the EArS reaction?

Lecture 13, Chapter 25.1-25.4

1. Memorize the structure of D-glucose in its Fischer projection. You do not need to know the structures of any other monosaccharide. Those will be given.
2. Be familiar with the Fischer projections but don't worry about the rotation of Fischer projections, which often causes more confusion than it's worth!
3. Complete #1-4 of the carbohydrate nomenclature worksheet before lecture 13.

Lecture 14, 25.5

1. What is a hemiacetal? What does it mean for two compounds to be anomers?
2. Draw the mechanism for the intramolecular cyclization of D-glucose. You will not be tested on this mechanism specifically, but it is good to know! You may be tested on a similar mechanism (hemiacetal or acetal synthesis).
3. Complete #5-6 of the carbohydrate nomenclature worksheet before lecture 14.

Lecture 15, Chapter 25.6

List the different reactions of sugars – which functional groups react and what new functional groups can be introduced? (skip phosphorylation)

Lecture 16, Chapter 26.1-26.2

1. Be able to identify whether an amino acid side-chain is neutral, polar, acidic, or basic. You do not need to memorize amino acid structures for the exam.
2. How many acidic protons does each type of amino acid have (neutral, acidic, basic)?
3. Practice drawing alanine in its fully protonated (acidic), zwitterionic (neutral), and fully deprotonated (Basic) forms.

Lecture 17, Chapter 26.3-26.5, 26.7

Skipping the amidomalonate synthesis

1. Which reactions in section 26.3 have you learned previously in the CHEM 8 series? Draw those reaction mechanisms to refresh your memory.
2. Practice drawing a simple tripeptide containing three alanine residues. Do the same with three valine residues.

Lecture 19, Chapter 27.1-27.3 and just the first bit of 27.5

1. Be able to draw and identify saturated and unsaturated fatty acids, triacylglycerols, and phospholipids. Fatty acid structures will be given from Table 27.1 on exams.
2. Be able to draw the hydrolysis products of triacylglycerols and phospholipids.
3. Read only the first two paragraphs of section 27.5 to get an idea of what terpenes and terpenoids are. You can look forward to learning about the metabolism of terpenes in CHEM 109!