Midterm 2 Review Key

[Sourced from Smith: Organic Chemistry 6th Edition]

1. Draw the products formed when the α, β-unsaturated ketone is treated with each reagent. Ignore stereochemistry. (17.40)


   
   ![Ketone reduction](image)

   b. Catalytic hydrogenation of ketone: reduction of the C=C bond

   
   ![Catalytic hydrogenation](image)

   c. Catalytic hydrogenation of ketone: reduction of C=C and C=O bonds to form alcohol

   
   ![Catalytic hydrogenation alcohol](image)

   d. Reaction of organometallic reagents with a ketone: addition of methyl group and hydrogen from water across the C=O bond.

   
   ![Organometallic reaction](image)

   e. Reaction of organometallic reagents with a ketone: addition of r group as well as hydrogen from the water across the C=O bond.
2. Draw the stepwise mechanism for the following reaction. (17.52)

3. Draw a stepwise mechanism for the following reaction. (17.55)
4. Outline a synthesis of each Wittig reagent from Ph₃P and an alkyl halide

   a. 
   
   \[
   \text{Ph}_3\text{P} + \text{BuLi} \rightarrow \text{Ph}_3\text{P} = \text{Bu}^- 
   \]

   b. 
   
   \[
   \text{Ph}_3\text{P} + \text{BuLi} \rightarrow \text{Ph}_3\text{P} = \text{Me}^- 
   \]

   c. 
   
   \[
   \text{Ph}_3\text{P} + \text{BuLi} \rightarrow \text{Ph}_3\text{P} = \text{Ph}^- 
   \]

5. **Cyanohydrins:** Draw out the products of each reaction. Keep potential stereoisomers in mind.

   a. 
   
   \[
   \text{NaCN} \rightarrow \text{HO} - \text{CN} + \text{HO} - \text{CN} 
   \]

   The cyanide anion will perform a nucleophilic attack on the carbonyl, leading to addition. Keep in mind that this forms a new stereogenic center.

   b. 
   
   \[
   \text{} 
   \]
This question asks for the hydrolysis of a CN group, the mechanism of which isn’t required but what matters is that it changes the CN to a COOH.

**Imine/Enamines**

5. Draw the product formed when the following molecules react with i) MeNH$_2$ ii) Et$_2$NH in catalytic acetic acid

a. 

![Diagram](image)

i) Acetic acid is important for protonating the O on acetone, leading to the carbonyl carbon being electrophilic enough for MeNH$_2$ to perform a nucleophilic attack on the carbon. Ultimately, a C=N double bond replaces the C=O double bond.

ii) Same as with (i) but at the end the C=N double bond leads to a positively charged N, so a deprotonation of a carbon adjacent to the C=N carbon leads to electrons being pushed to the N, neutralizing it.

b. 

![Diagram](image)

i) MeNH$_2$ performs a nucleophilic attack on the carbon after protonation of O. Ultimately, a C=N double bond replaces the C=O double bond.

ii) Same as with (i) but at the end the C=N double bond leads to a positively charged N, but there is no H on carbons adjacent to the C=N carbon, thus the enamine remains in its positive form.
Synthesis

6. What carbonyl and amine are needed to produce the following products?

a. ![Diagram a]

b. ![Diagram b]

In imine/enamine formation, the C=O bond is replaced by N-H. In the case of enamine, deprotonation of a carbon adjacent to the C=N carbon pushes electrons to the N, neutralizing it.

7. What Wittig reagent and carbonyl are needed to produce the following alkenes? Choose the preferred route.

a. ![Diagram a]

b. ![Diagram b]
In the most simple sense, \( \text{Ph}_3\text{P} = \text{R} \) replaces the \( \text{C} = \text{O} \) bond with a \( \text{C} = \text{C} \) bond. The preferred path is one in which the phosphonium ylide is least substituted. This is because in synthesizing the Wittig reagent, \( \text{P} \) performs an \( \text{Sn2} \) attack on an alkyl halide. The less substituted the alkyl halide, the more efficient the synthesis.

**Mechanisms**

8. Draw out the stepwise mechanisms for the following reactions
   a.
Spectroscopy
9. Draw out the compound given the molecular formula and NMR spectra
   a. $\text{C}_{10}\text{H}_{12}\text{O}$

There are 8 carbon signals whereas the molecule formula has 10 carbons. This is a big indicator that there are symmetrical carbons on the molecule. A carbon-NMR shift above 190 ppm indicates a ketone or aldehyde. Now observe the H-NMR splitting: triplet 3H must mean terminal $\text{CH}_3$, quartet 2H is a methylene, singlet 2H is a methylene with no adjacent C-H, and the multiplet 5H is characteristic of 5 benzene hydrogens.
10. Circle the compound that corresponds to the following NMR spectra.

b.
Count the number of carbon signals. There are 5 whereas (b) has 6. Eliminate (b). (c) and (e) can be eliminated because aldehydes and ketones have a C-NMR chemical shift of 190+ ppm. That is not observed, thus cross out (c) and (e). Now compare the H-splitting for (a) and (d): singlet 1H at 5 ppm is O-H, the two singlet 3H’s are terminal CH₃ with no adjacent C-H; at this point, the only structure that corresponds to this is (d).