Answers to Problem Set 3

Question 1. Provide reagents (by each arrow) that will accomplish the following transformations. *Yes, this is a review of last semesters material!*

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{H}_2\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

1. BuLi (or equivalent strong base)
2. CH\(_3\)I

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{H}_2\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

1. BH\(_3\)
2. H\(_2\)O\(_2\)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{H}_2\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

1. O\(_3\)
2. H\(_2\)O\(_2\)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{H}_2\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

1. H\(_2\)SO\(_4\), NaCl or TsCl followed by NaCl
Question 2. Label the indicated hydrogen atoms as homotopic, enantiotopic, or diastereotopic.

- Homotopic
- Enantiotopic
- Diastereotopic

Question 3. Rank the following carbocations from most to least stable.

- Most stable – resonance between 1° and 3° carbocations
- Resonance between 1° and 2° carbocations
- Localized 1° carbocation
- Least stable – a vinyl cation. This has no resonance stabilization and the cation is forced into an sp² orbital
Question 4.  

a) Provide the major product of the reaction shown below. *Assume that only one molecule of HCl adds to the cyclohexadiene.*

![Reaction Diagram](image)

b) Draw all the possible cationic intermediates for the reaction. Which of these are resonance forms? Which structure is most stable? Least stable?

![Cationic Intermediates](image)

Chloride attack here gives the major product: 

- 2° carbocation, not resonance stabilized, disubstituted olefin – *Least stable*
- Resonance between a 3° and a 2° carbocation – *Most stable*
- Resonance between two 2° carbocations
- 2° carbocation, not resonance stabilized, trisubstituted olefin
  *(If you said this was the least stable, you are close enough)*
Question 5. Crotonaldehyde (A) is much more stable than methyl ketene (B).

\[ \text{Chem 242} \]

\[ \text{Spring 2008} \]

a) Draw molecular orbitals, including nodes and orbital phases, for crotonaldehyde.  
*Note: these orbitals are drawn looking down from the “top” (they are all p-orbitals)*

\[ \text{A} \quad \text{B} \]

b) Draw the major resonance form(s) of methyl ketene.  Are the double bonds in methyl ketene considered conjugated?  Why or why not?

\[ \text{The double bonds are not conjugated, they are orthogonal (twisted 90° relative to each other)} \]
c) Explain briefly the difference in stability between A and B.

*Crotonaldehyde contains a 4-electron conjugated π-system, methyl ketene has no conjugation between π-bonds. Also, the resonance structure of methyl ketene shown on the right in part (b) is not very stable due to the vinyl carbocation. Therefore, the oxygen gains very little electron density from the adjacent carbon atom.*

Question 6. Show how you can accomplish the following multistep transformation (yup, this is a hard one, but somewhat similar to your lab experiment…).