Exam 3 Spring 2014

Name Key ________________________________________ Room ______

Student ID ________________________________________ Seat Number ______

Circle One 11:15 AM Class 12:20 PM Class

The exam consists of 8 questions on a total of 9 pages.

1. ____/20
2. ____/20
3. ____/10
4. ____/10
5. ____/12
6. ____/8
7. ____/10
8. ____/10

Regrading: All requests for regrades must be submitted in writing within 48 hours of the return of the exam. You must explicitly state what has been misgraded and why it is an error. The entire exam will be regraded, which could result in points being added or deducted overall.
1. (20pts) Provide reagents or starting materials necessary for 5 of the following 6 transformations. CLEARLY MARK the one you do not want graded or else the first five will be graded. More than one step may be necessary.

- **2-butyne**
  \[ \text{2-butyne} \xrightarrow{2 \text{ eq } \text{HBr}} \xrightarrow{\times 5 \text{ HBr}} 2,2\text{-dibromobutane} \]

- **3,3-dimethylbut-1-ene**
  \[ \text{1. O}_3 \]
  \[ \xrightarrow{2. \text{DMS}} \text{3,3-dimethylbutan-2-ol} \]

- **2,2-dibromobutane**
  \[ \xrightarrow{\times 5 \text{NaBH}_4} \xrightarrow{\text{H}_3\text{O}^+} \]

- **but-1-yne**
  \[ \xrightarrow{\times 5 \text{NaBH}_4} \xrightarrow{\text{H}_2\text{O}} \text{but-1-yne} \]
2. (20pts) Predict the MAJOR product(s) of 5 of the following 6 reactions. CLEARLY MARK the one you do not want graded or else the first five will be graded. Include proper stereochemistry, and indicate if the enantiomer also forms.

1. H₂, Lindlar's cat.
2. mCPBA
3. H₃O⁺

methylocyclopentane → Br₂, light

H₂, Pd

Br₂

Ph

Br₂, CH₃OH

1. BH₃ THF
2. H₂O₂, HO⁻
3. (10pts) Provide arrow mechanisms, including all intermediates, for the formation of this product:

Based on your mechanism, redraw the product with appropriate stereochemistry:

Based on your mechanism, draw a second product that you would expect to see form.
4. (10pts) Draw the product(s) of this reaction, including stereochemistry. Then provide an arrow mechanism, including all intermediates, for the reaction.

In ONE SENTENCE, how does your mechanism explain the STEREOCHEMISTRY of the reaction?

Both enantiomers form (mixture) because $\text{Nu}^-$ can attack on both sides of planar carbocation equally well. 

In ONE SENTENCE, how does your mechanism explain the REGIOCHEMISTRY of the reaction?

The $\text{Cl}^-$ is added to the more substituted carbon (or $\text{H}$ added to less substituted or Markovnikov is observed because the more stable carbocation forms (can also include hyperconjugation, Hammond, etc.)
5. (12pts) Provide all necessary reagents for the following multistep syntheses, starting from the given material. You may use any additional organic or inorganic reagents you need. Although grading will be based on reagents used, showing intermediates can lead to partial credit.

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]

\[ \text{+2} \quad \text{+2} \]
6. (8pts) In ONE SENTENCE, explain why this reaction will not work as drawn:

1. tBuO'K⁺
2. EtBr

The base is not strong enough to deprotonate an alkyne.

In ONE SENTENCE, explain why this reaction will not work as drawn:

1. BH₃ THF
2. H₂O₂, HO⁻

These reagents lead to a syn addition of -H and -OH, giving the wrong stereochemistry.
7. (10pts) Provide a full arrow mechanism for both steps of the following transformation.

Step 1 mechanism:

Step 2 mechanism:

-1 if acid/H₂O in first step
8. (10pts) Provide all reagents necessary for this multistep synthesis. You may use the starting material below and acetylene as your only other source of carbon, but you may use any other reagents of your choice.

Could also do Anti-Mark with -OH, then TSCI.

+3 minimum if any one key reaction correct, and only using acetylene
+7 minimum if both key C-C bonds formed