CHEM 5.12
PROBLEM SET #7 (this really is PS#7 and the last one was actually PS#6!)
Due in Friday April 11th at 4 pm

1. (3 points total) a. For the following compounds estimate the pKₐ of the hydrogen indicated by the arrow and rank the compounds from the MOST acidic to the LEAST acidic.

\[
pKₐ = \begin{cases} 
10 & \text{A} \\
5 & \text{B} \\
2.5 & \text{C} \\
16 & \text{D} \\
35 & \text{E} 
\end{cases}
\]

MOST ACIDIC: B A D C E LEAST ACIDIC

b. You need to select a base to deprotonate ethyne. Using the information derived above - what base would you select if you could choose the conjugate base of any of the acidic species shown above?

2. (3 points) For the following reaction show the stepwise mechanism and identify the different isomeric products that are formed. You may want to build a model of the methylicyclohexene as you think about how the mCPBA will react and then when you think about how the product of that reactions reacts.

1. mCPBA
2. H⁺/H₂O

Remember epoxide protonated for attack.

Remember same.
4. (6 points) Provide a detailed stepwise mechanism to account for the following reactions.

\[
\text{CO}_2\text{H} \xrightarrow{\text{I}_2/\text{NaHCO}_3} \text{O} \quad \text{for iodonium}
\]
\[
\text{for ring opening}
\]

\[
\text{H} = \text{B}-\text{H} \quad \text{H} \quad \text{B} \quad \text{H} \quad \text{B} \quad \text{H}
\]

\[
\text{B}_2\text{H}_6 \xrightarrow{\text{BH}_3} \text{O} \quad \text{B to less substituted end}
\]

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{H}_2\text{O}} \text{ess. H} \quad \text{H} \quad \text{O-OH}
\]

\[
\text{HOOH} \quad \text{for tautomerism}
\]

\[
\text{H}_2\text{O} / \text{H}_2\text{O}_2 \quad \text{NaOH} / \text{H}_2\text{O}_2
\]

\[
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\]
3. (8 points) Design syntheses of compounds I and II. The pool of carbon-containing starting materials that you can use are shown in the square brackets. You may use any other common reagents. A clear retrosynthetic analysis will help you plan the synthesis.

I. Retrosyn:

\[ \text{Synthesis:} \quad \overset{\text{N_2^+ \text{NH}_2}}{\text{H-C\equiv C-H}} \rightarrow \quad \overset{\text{N_2^+ \text{NH}_2}}{\text{H-C\equiv C-\Theta}} \rightarrow \quad \overset{\text{Lindlay's catalyst}}{\text{H-C\equiv C-H}} \quad \text{H}_2 \rightarrow \quad \text{I} \]

II. Retrosynthesis:

\[ \text{Synthesis:} \quad 1. \text{Na}_2\text{NH}_2 \quad \overset{\text{N_2^+ \text{NH}_2}}{\text{H-C\equiv C-H}} \quad 2. \overset{\text{Br}}{\text{Cyclohexanone}} \quad 3. \overset{\text{H}_2\text{O}}{\text{OH}} \rightarrow \quad \overset{\text{N_2^+ \text{NH}_2}}{\text{H-C\equiv C-H}} \quad 1. \text{Na}_2\text{NH}_2 \quad 2. \overset{\text{Br}}{\text{Cyclohexanone}} \quad 3. \overset{\text{H}_2\text{O}}{\text{OH}} \rightarrow \quad \text{II} \]