CHEM 3331, Spring 2011
Professor Walba
First Hour Exam
February 10, 2011

scores:

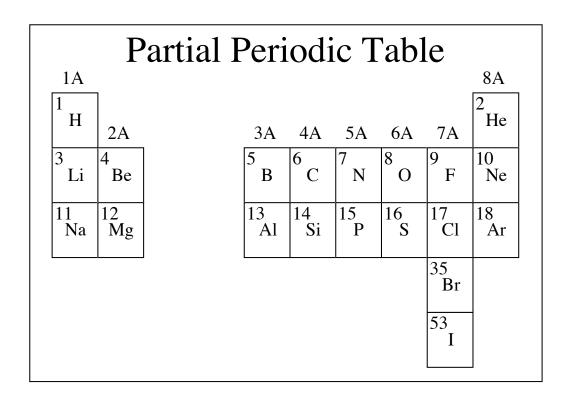
1) 20
2) 20
3) 20
4) 20

5) 20

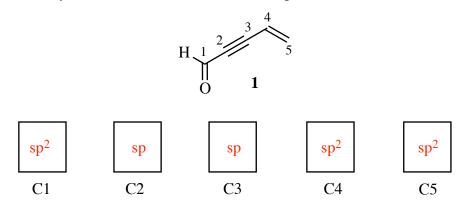
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CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.
Name (printed): Key
Signature:
Recitation TA Name:
Recitation day and time:
This is a closed-book exam. The use of notes, models, calculators, scratch paper, or any other paraphernalia will not be allowed during the exam. Please put all your answers on the test. Use the backs of the pages for scratch.

## PLEASE read the questions very carefully!



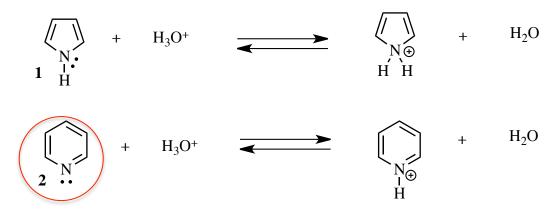
1) (20 pts) a) Indicate the hybridization of each carbon in compound 1.



b) Circle each of the aromatic compounds in the following list. Following the common convention, H atoms are shown on heteroatoms, but not on carbon.



c) Pyrrole (1) and pyridine (2) differ greatly in their basicity. In the following Bronsted acid-base reactions of 1 and 2, the compounds are acting as bases ( $H_3O^+$  is the acid). Circle the compound that has the larger  $K_{equ}$  going left to right (i.e. the stronger base).



d) Briefly explain your answer to part c) above.

Pyrrole is a very weak base because protonation of the lone pair breaks the aromaticity of the pyrrole ring. Protonation of the lone pair on pyridine does not break the aromaticity.

2) (20 pts) Give the single major product of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac."

a) 
$$\longrightarrow$$
 CH<sub>3</sub>  $\xrightarrow{\text{H}_2, Lindlar catalyst}}$ 

b) 
$$SO_3, H_2SO_4$$
  $SO_4$  OH

Reaction c) above is irreversible at -80°C

d) Cl 
$$\xrightarrow{a) AlCl_3}$$
  $\xrightarrow{b) H_2O \text{ workup}}$ 

e) 
$$\Delta$$
 (heat)  $H$  rac

3) (20 pts) Propose reagents for accomplishing the following transformations. NOTE: more than one step may be required! Try to make your synthesis efficient (i.e. the desired product should be the major product, and generally a shorter synthesis is better than a longer one). You must use the starting material given; you may use any other reagents you need.

$$Br_2, FeBr_3$$

4) (20 pts) a) 3-methyl-1-butyne (1) reacts with a hindered borane 2 (R = large group) in tetrahydrofuran to give compound 3. Give the structure of compound 3, showing stereochemistry if appropriate.

b) When compound 3 from part a) is allowed to react with hydrogen peroxide/sodium hydroxide, the enol 4 is initially produced. This, however, is not the final product of the reaction. Give the structure of the product of this reaction, compound 5.

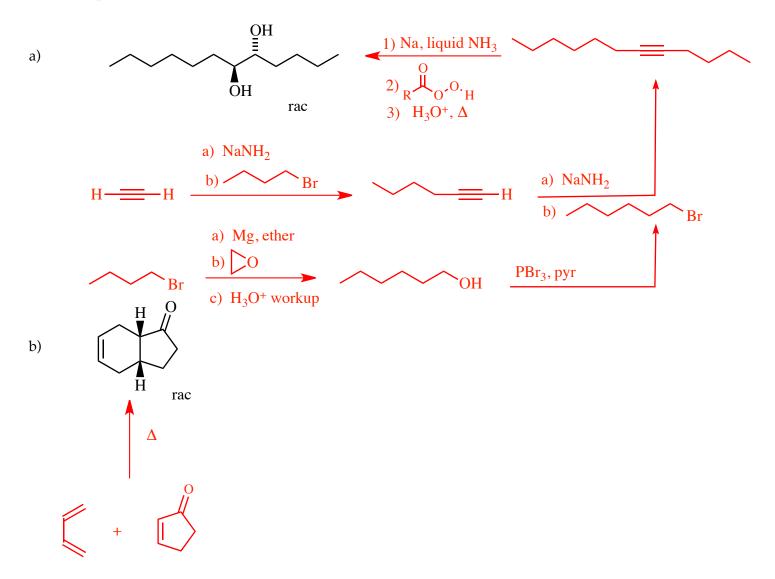
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$$\xrightarrow{a) H_2O_2, NaOH}$$
  $\xrightarrow{OH}$   $\xrightarrow{A}$   $\xrightarrow{B}$   $\xrightarrow{A}$   $\xrightarrow{A}$ 

c) The enol 4, and product 5 are rapidly interconverted with either acid or base, though product 5 is strongly favored in the equilibrium. Propose an arrow-pushing mechanism for the equilibration of 4 and 5 in aqueous acid ( $H_3O^+$ ).

## 4) - Continued

Propose an arrow-pushing mechanism for each of the following reactions.

5) (20 pts) Propose a synthesis of each of the following targets, starting with benzene and/or any other organic molecules containing **five (5) carbons or less**. You may use any necessary inorganic reagents. Try to make your synthesis efficient (i.e. the target should be produced in the highest possible yield). More than one step may be required.



## 5) – Continued

