Exam 2
Chemistry 223
March 23, 2010

Do not open or begin this exam until instructed. This exam consists of 8 pages plus the cover page. Before starting the exam check the number of pages in your exam. This exam is worth 100 pts and includes 8 questions. Budget your time wisely. Only legible answers written on the exam will be considered for grading. All pertinent information needed for the exam is given. Notes, calculators, models, computers and textbooks are not permitted. This exam is administered under the Wake Forest Honor Code. Good Luck and remember to put your name on the line provided below.

Name  KEY
---------------------------------------------------------------
1. (12 pts) Provide a proper IUPAC name for the following molecules:

2. metaxy-5-bromobenzoyl chloride

\[ \text{Br} \hspace{1cm} \text{O} \]
\[ \text{Cl} \hspace{1cm} \text{OCH}_3 \]

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \]

\[ \text{R} - \text{4-methyl-7-octenoic acid} \]

Provide structures for the following names.

Z-4-fluoro-3-pentenal

2,2,3,3-tetramethyl cyclopentanone
2. (12 pts) Propose a synthetic route for the following molecules from the given starting materials and reactions you have learned. You can use more than one molecule of the given starting materials. The pKa of the conjugate acids of some common bases that you may need to form anions for these questions are H$_3$O$^+$ = -1.7, CH$_3$CO$_2$H = 4.7, phenol = 10, CH$_3$OH = 15.5, H$_2$O = 15.7, NH$_3$ = 36, H$_2$ = 37, and CH$_4$ = 50.

![Chemical structures and reactions diagram]

and any one carbon compounds and Grignard reactions
3. (11 pts) Provide a structure for the following molecule (C₁₀H₁₂O₂) based on the given NMR and IR data.

IR
- absorbance 3100-3000 cm⁻¹, strong
- absorbance at 2900 cm⁻¹, strong
- absorbance at 1735 cm⁻¹, strong
- absorbance at 1080 cm⁻¹, strong

¹³C NMR
- total of eight resonances, 175, 132, 125, 122, 121, 60, 45, 20 proton decoupled

¹H NMR
- 7.40-7.10 (multiple peaks, relative area 5)
- 3.60 (quartet, relative area 2)
- 2.60 (singlet, relative area 2)
- 1.80 (triplet, relative area 3)

Note: By determining the number of unsaturations and correctly identifying functional groups or fragments in this molecule, partial credit may be achieved.
4. (12 pts) Provide the product or products for the following Grignard, organocuprate or Wittig reactions (or preparation of these reagents). Show all stereochemistry. No reaction is a possible answer.

\[
\begin{align*}
\text{1. CH}_3\text{MgBr} & \quad \xrightarrow{\text{1. } (\text{CH}_3)_2\text{CuLi}} \\
\text{2. H}_2\text{O} & \quad \xrightarrow{\text{1. Ph}_3\text{P}=\text{CH}_2} \\
\text{2. H}_2\text{O} & \\
\end{align*}
\]
(12pts) Provide a detailed electron pushing mechanism to explain the following two reactions: a) acid-catalyzed hydrolysis of an amide and b) the formation of an imine from a ketone and amine reaction.

\[ \text{Acid-catalyzed hydrolysis of an amide} \]

\[ \text{Formation of an imine from a ketone and amine} \]
6. (14 pts)

The reaction of a ketone with hydrazine (NH₂NH₂) gives a:

Imine  oxime  hydrazone  enamine

Conjugation has what effect on the IR frequency of a carbonyl group?

None  Increases frequency  Decreases frequency  Cancels out

Aldehyde and ketone carbonyl carbons appear in what range in the ¹³C NMR spectrum?

10-20 ppm  100-120 ppm  150-155 ppm  190-210 ppm

Circle the product of the reaction of acetone with hydroxylamine (NH₂OH):

\[
\begin{align*}
\text{O} & \quad \text{NCH}_3 & \quad \text{NOH} & \quad \text{NH} \\
\end{align*}
\]

The reaction of cyanide ion with an aldehyde/ketone forms a:

Hydrate  ether  ketal  cyanohydrin

Circle the acetal/ketal.

\[
\begin{align*}
\text{OH} & \quad \text{OCH}_3 & \quad \text{CH}_3\text{O} \cdot \text{OCH}_3 & \quad \text{phenyl} \\
\end{align*}
\]

In terms of H-bonding abilities, aldehydes and ketones can be described as H-bond:

donors  acceptors  both  neither
7. (12 pts) Provide reagents required for the following conversions.

Use a few words, structures, equations (whatever you need) to explain why the tertiary alcohol forms in the first reaction but not the second. For the second reaction, predict whether no reaction occurs or if other products are formed (and if so, what are they). You do not need to draw a full mechanism for this but your answer must clearly explain why one works and one doesn’t.

* Grignard cannot add to salt of acid (2nd run)
  Ion add to ether, no acid base reaction
8. (14 pts) Answer the following questions regarding the synthesis of the ester labeled compound C from the carboxylic acid (Compound A) and alcohol (Compound B).

\[
\text{Compound A} \quad + \quad \text{Compound B} \quad \rightarrow \quad \text{Compound C}
\]

For Compound A:

\[
\text{MgBr}
\]

For Compound B:

\[
\text{Br} \quad \rightarrow \quad \text{CN} \quad \rightarrow \quad \text{OH} \quad \rightarrow \quad \text{HO-}
\]

Circle the reagent required to convert A and B to Compound C.

LiAlH₄ \quad \text{LDA/THF} \quad \text{H⁺ catalyst} \quad \text{KOH/H}_2\text{O}

Circle the reagent required to convert D to Compound A.

\[
\text{CO₂} \quad \text{NaCN} \quad \text{MCPBA} \quad \text{H}_3\text{O⁺}
\]

Circle the reagent required to convert E to Compound F.

\[
\text{CO₂} \quad \text{NaCN} \quad \text{NaBH₄} \quad \text{CH₃CN}
\]

Circle the IUPAC name of Compound F.

1-cyanobutane \quad \text{nitrilepropane} \quad 1-pentynimine \quad \text{butanecnitrile}

Circle the reagent required to convert F to Compound G.

DIBAL \quad \text{CH₃MgBr} \quad \text{H}_3\text{O⁺/heat} \quad \text{Ag₂O}

Circle the major IR stretch of Compound G.

\[
3750 \text{ cm}^{-1}, \text{ sharp} \quad 1200 \text{ cm}^{-1}, \text{ murky} \quad 3500-2500 \text{ cm}^{-1}, \text{ broad} \quad 1450 \text{ cm}^{-1},
\]

Circle the reagent required to convert G to Compound B.

LiAlH₄ \quad \text{NaOH/H}_2\text{O/heat} \quad \text{heat} \quad \text{Mg}