EXAM #4

Name: ____________

ID#: ________________

Check your exam to be sure it is complete. There are eight questions in this exam. It is worth 100 points. To receive full credit for your submissions, make sure you do your own work. Read each question carefully, and answer in clearly legible and coherent English. Use the back of the page for additional space if needed. Partial credit will be given, so show your work. Don’t fall in love with individual problems. Do the ones first which you can do easily. Pace yourself. Good luck!

N. Totah

1. ____________ (of 5)
2. ____________ (of 6)
3. ____________ (of 10)
4. ____________ (of 10)
5. ____________ (of 38)
6. ____________ (of 8)
7. ____________ (of 11)
8. ____________ (of 12)

Total: ____________ (100)
1. (5 points) Give IUPAC names for the following compounds:

a. \[
\begin{array}{c}
\text{N-butylpentylamine} \\
\text{or} \\
\text{N-butylpentanamine}
\end{array}
\]

b. \[
\text{(R)-2-aminoheptanal}
\]

2. (6 points) Clearly explain how you could distinguish between the compounds below by IR spectroscopy. For full credit, indicate what you would expect to see for each compound. Be specific. Cite numerical values/ranges to support your claims.

Can differentiate all by absorbances in the 3300-3500 cm\(^{-1}\) region:

All absorbances in the 3300-3500 cm\(^{-1}\) region:

A: 2° amine: N-H absorbance (single band) expected

B: 1° amine: N-H absorbance (two bands) expected

N-H bands will be sharp, and of moderate to weak intensity

C: O-H: strong, broad absorbance expected
   (as compared to A and B)
3a. (4 points) Rank the following compounds in order of decreasing basicity. Label the most basic compound (1) and the least basic compound (4). Place the number corresponding to the relative basicity of each compound in the blank below.

\[
\begin{array}{cccc}
\text{NO}_2 & \text{CH}_3 & \text{C}_6\text{H}_5 & \text{CH}_3 \\
\text{NH}_2 & \text{NH}_2 & \text{NH}_2 & \text{NH}_2 \\
1 & 2 & 3 & 4
\end{array}
\]

3b. (4 points) Clearly identify (draw in) all of the acidic hydrogens in the compounds below. If there are no acidic hydrogens, write "none" below the structure.

\[
\begin{array}{cccc}
\text{CH}_3 & \text{O} & \text{H} & \text{H} \\
\text{O} & \text{O} & \text{O} & \text{O} \\
\text{H} & \text{H} & \text{H} & \text{H} \\
\text{none} & \text{none} & \text{none} & \text{none}
\end{array}
\]

3c. (2 points) Circle the compound below that is NOT a Michael acceptor.

\[
\begin{array}{cccc}
\text{CH}_2\text{CN} & \text{CH}_2=\text{CHCO}_2 & \text{CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2 & \text{CH}_2=\text{CHOCH}_3
\end{array}
\]
4a. (6 points) Write a complete, stepwise mechanism for the following transformation. Use curved arrows to denote electron flow. Be sure your answer clearly accounts for the formation of both enantiomers of the product.

\[
\begin{align*}
\text{optically active} & \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{racemic} \\
\end{align*}
\]

Mechanism:

\[
\begin{align*}
\text{protonation from back} & \quad \xrightarrow{\text{H}^+} \quad \text{protonation from front} \\
\end{align*}
\]

4b. (4 points) Draw all resonance structures for the enolate that is formed when compound A reacts with EtONa in ethanol.

\[
\begin{align*}
A & \quad \overset{-\text{OCH}_3}{\text{O}} \\
\text{enolate} & \quad \overset{-\text{OCH}_3}{\text{O}} \\
\end{align*}
\]
5. (38 points) Predict the major product(s) for the following reactions. Assume reagents are present in equimolar amounts unless otherwise indicated. Clearly depict any stereochemistry. "No Reaction" is a possible answer. CAUTION! Don't confuse reactions that will occur slowly with those that will not occur!

a. 

\[
\begin{align*}
\text{Br}_2, \text{PBr}_3 & \\
\text{H}_2 \text{O} & \\
\end{align*}
\]

b. 

\[
\begin{align*}
\text{NO}_2 & \\
\text{H}_2 / \text{Pt} & \\
\text{EtOH} & \\
\end{align*}
\]

product(s) of step 1

\[
\begin{align*}
\text{Cl} & \\
\text{pyridine} & \\
\end{align*}
\]

(step 2)

c. 

\[
\begin{align*}
\text{NaOEt} & \\
\text{EtOH, 0°C} & \\
\end{align*}
\]

d. 

\[
\begin{align*}
\text{NaN}_3 & \\
\text{LiAlH}_4; \text{H}_2\text{O} & \\
\end{align*}
\]
e. $\text{O} \quad \text{1. LDA, } -78^\circ\text{C} \quad \text{PhCH}_2\text{Br} \quad \text{O} \quad \text{Ph}$

f. $\text{2} \quad \text{O} \quad \text{1. NaOEt} / \text{EtOH} \quad \text{EtOH} \quad \text{O} \quad \text{Et}$

$\quad \text{2} \quad \text{O} \quad \text{EtOH} \quad \text{2. H}_3\text{O}^+ \quad \text{EtOH} \quad \text{O}$

$\quad \text{2} \quad \text{H}_3\text{O}^+ \Delta \quad \text{2. H}_3\text{O}^+$

h. 2

\[
\begin{align*}
\text{b} & \quad \text{NaOEt} \quad \text{EtOH}, \Delta \\
\text{O} \quad \text{EtOH} \quad \text{O} \quad \text{EtOH}, \Delta
\end{align*}
\]

i. 2

\[
\begin{align*}
\text{a} & \quad \text{Cl}_2 \quad \text{CH}_3\text{CO}_2\text{H} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]
j. \[
\text{CH}_3NH\text{H} \quad \begin{array}{c}
\text{Cl} \\
\text{AlCl}_3
\end{array} \quad \text{No Reaction}
\]

k. \[
\text{EtO}_2\text{C} \quad \text{NaOEt / EtOH} \quad \text{EtO}_2\text{C} \quad \text{EtO}_2\text{C}
\]

\text{(step 1)}

\[
\text{product(s) of step 1} \quad \text{H}_3\text{O}^+ \quad \text{EtO}_2\text{C} \quad \text{EtO}_2\text{C}
\]

\text{(step 2)}

l. \[
\text{PhCHCl} \quad 1. \text{NaN}_3 \quad \text{PhCH}_2\text{NH}_2
\]

2. \(\Delta\) 

3. \(\text{H}_2\text{O}\)

m. \[
\text{EtO}_2\text{C} \quad \text{1. NaOEt (excess), EtOH} \quad \text{EtO}_2\text{C}
\]

\text{Br} \quad \text{Br}

2. \(\text{H}_3\text{O}^+, \Delta\)
Name: ________________________________

n.

\[
\text{NH}_2
\]

\[
\text{Cl}
\]

1. KOH
2. Cl
3. KOH, H\text{2O}

(step 1)

product(s) of step 1

1. CH\text{3I} (excess)
2. Ag\text{2O}, H\text{2O}, \Delta

(step 2)

o.

\[
\text{CH}_3
\]

1. NaOMe / MeOH
2. H\text{3O}^+

p.

\[
\text{HSO}_4^-
\]

\[
\text{OCH}_3
\]

\[
\text{OCH}_3
\]

\[
\text{Cl}
\]

\[
\text{N} \equiv \text{N}
\]

\[
\text{N} \equiv \text{N}
\]

\[
\text{Cl}
\]

\[
\text{OCH}_3
\]

\[
\text{OCH}_3
\]

\[
\text{OCH}_3
\]

\[
\text{OCH}_3
\]
6. (8 points) The following reactions will not proceed as written. Clearly explain the problem. Indicate what product(s), if any, you expect to see, and explain how you would modify the reaction conditions such that the products shown will be isolated in high yield. Be specific.

a. 

\[
\begin{align*}
& \text{A} \quad \text{B} \\
& \begin{array}{c}
\text{NH}_2 \\
\text{C}_6\text{H}_5 \end{array} \quad \begin{array}{c}
\text{CH}_3\text{CH}_2\text{-I} \\
(1 \text{ mole}) \quad (1 \text{ mole})
\end{array} \\
& \quad \xrightarrow{1. \text{ mix}} \quad \xrightarrow{2. \text{ NaOH}} \quad \text{C} \\
& \begin{array}{c}
\text{H} \\
\text{NCH}_2\text{CH}_2\text{CH}_3
\end{array}
\end{align*}
\]

A mixture of compounds will be formed because the product amine C will react again with B to give polyalkylation products.

High yields of the 2° amine C can be obtained if the starting material A is used in large excess.

b. 

\[
\begin{align*}
& \text{D} \quad \text{E} \\
& \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH} \quad \text{CH}_3\text{CH}_2\text{-Li} \\
(1 \text{ mole}) \quad (1 \text{ mole})
\end{array} \\
& \quad \xrightarrow{\text{THF \ -78°C}} \quad \text{F} \\
& \text{HO} \quad \text{O}
\end{align*}
\]

In the presence of LDA the enolate of D will form quickly and quantitatively.

No ketone D will remain in solution to react with the enolate, so no aldol reaction is possible.

Problem can be solved by using a weaker base like NaOEt so the concentration of enolate is low and some ketone is still present in the reaction mixture.
7. (11 points) Compound A (C₃H₆O) is a neutral compound that undergoes self-condensation in the presence of NaOEt in EtOH at 40°C to give a new compound B (C₆H₁₀O). Compound B shows 6 signals in the $^{13}$C NMR ($\delta$ 198, 154, 124, 32, 28, 20). Upon hydrogenation (H₂, Pd/C), compound B gives compound C. Treatment of compound C with I₂ in the presence of base (e.g. I₂, NaOH, H₂O) results in the formation of a yellow precipitate. Further, compound C reacts with Me₂NH under reductive conditions (Me₂NH, NaCNBH₃) to give a new compound D that shows no diagnostic absorbances in the IR. However, when Compound D is treated with HCl, the IR shows strong peak at 2400 cm⁻¹. Using this information, determine the structure of compounds A - D. Show your work for full credit. As part of your answer, briefly indicate how each piece of spectroscopic data or chemical test supports the structures you propose.

$^{13}$C NMR: compound B has 6 unique carbon atoms

- $\delta$ 198 - consistent w/ketone
- $\delta$ 154, 124 - consistent with double bond

Iodoform test: Compound C is a methyl ketone

IR: Compound D is a 3° amine
8. (12 points) Show how you would carry out the following transformations, avoiding product mixtures if possible. Use any organic or inorganic reagents that you need. Show all reagents and intermediate products.

a. 5

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{Et} & \quad \text{Et} \\
\text{OH} & \quad \text{CH}_2=\text{CH}_2
\end{align*}
\]

\[\text{EtO} + \text{NaOEt/EtOH} \rightarrow \text{CH}_2=\text{CH}_2\]

\[\text{EtOEt} \xrightarrow{\Delta} \text{EtOEt} + \text{H}_3\text{O}^+\]

b. 7

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[\text{HNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ \quad \text{O} = \text{C} \quad \text{NaBH}_3\text{CN} \]

\[\text{KCN} \quad \text{CuCN} \rightarrow \text{CN} \quad \text{CN} \]

\[\text{1. LiAlH}_4 \quad \text{2. H}_2\text{O} \]

\[\text{NH}_2 \]