Exam 3  
Chemistry 223  
April 15, 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 (4 pts)       KEY

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

\[
\begin{align*}
\text{N}_2\text{N-dimethyl t-butylamine} \\
\text{di-n-butyl amine}
\end{align*}
\]

Provide structures for the following names.

Ethyl Z-2-butoenoate

R-1-phenyl-2-aminohexane
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 $\text{H}_3\text{O}^+ = 1.7$, $\text{CH}_3\text{CO}_2\text{H} = 4.7$, phenol = 10, $\text{CH}_3\text{OH} = 15.5$, $\text{H}_2\text{O} = 15.7$, EtOH = 17, diisopropylamine = 35, NH$_3$ = 36, H$_2$ = 37, and CH$_4$ = 50.

![Chemical structures and reactions diagram]

Using an acetoacetate synthesis and common electrophilic addition.

Using a Robinson annihilation.
3. (12 pts) Mixture of acetone (CH₃COCH₃) with excess benzaldehyde (PhCHO) in aqueous NaOH gives a new condensation product (C₁₇H₁₄O) with the following NMR and IR data. Propose a structure.

**IR**
- absorbance 3100-3000 cm⁻¹, strong
- NO absorbance at 2900 cm⁻¹
- no sp² C-H
- absorbance at 1665 cm⁻¹, strong (conjugated C=O)
- alkene

**¹³C NMR**
- total of 7 resonances, 190, 132, 125, 122, 121, 117, 115 proton decoupled

**¹H NMR**
- 7.40-7.10 (multiple peaks, relative area 5)
- 5.60 (doublet, relative area 1)
- 5.10 (doublet, relative area 1)
- alkene H, 2 identical

**Note:** By determining the number of unsaturations and correctly identifying functional groups or fragments in this molecule, partial credit may be achieved.

**Hint:** This product needs two aldol condensations to form.
4. (12 pts) Provide the product or products for the following reactions. Show all stereochemistry. No reaction is a possible answer.
5. (12 pts) Provide a detailed electron pushing mechanism to explain the following two reactions: a) a decarboxylation of a keto ester (show where all 3 products come from) and b) a Robinson annulation.
6. (12 pts)

An intramolecular Claisen condensation is a **what name**-condensation:

- [ ] Dieckmann
- [ ] Michael
- [ ] Robinson
- [ ] Gabriel

Which of the following is a negatively charged intermediate?

- [ ] Schiff Base
- [ ] Carbocation
- [ ] Enolate
- [ ] Enol

Amines are organic derivatives of what simple molecule?

- [ ] Water
- [ ] Ammonia
- [ ] Hydrogen sulfide
- [ ] Cyanide

A common solvent for LDA reactions is:

- [ ] Water
- [ ] Tetrahydrofuran
- [ ] Acetone
- [ ] Ethanol

Circle the secondary amine.

- \[ \text{[amino group]} \]
- \[ \text{[secondary amine]} \]
- \[ \text{[tertiary amine]} \]

By definition, tertiary amines with three different groups are:

- [ ] Chiral
- [ ] Meso
- [ ] Achiral
- [ ] Liquids
7. (12 pts) Provide reagents required for the following conversions.

Use a few words, structures, equations (whatever you need) to explain why phthalimide 1) is much less basic than triethylamine (pKa of protonated phthalimide = 1) and 2) why phthalimide only reacts once as a nucleophile with an alkyl halides (unlike primary amines).

1) phthalimide is less basic than other amines because the lone pair (needed) for basicity is involved in resonance. Therefore not used for bases.

2) phthalimide reacts with alkyl halides as an anion once it reacts once - cannot form another anion to react.
8. (12 pts)  For each of the following reactions

Provide the products of each acid-base reaction below

Using the pKa values given draw an arrow to show which side the equilibrium lies.

\[ \text{CH}_3\text{NH}_2 + \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{CH}_3\text{CO}_2\text{H} \]

\[ \text{HCl} + \text{C}_6\text{H}_5\text{NH}_2 \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{HCl} \]

\[ \text{O}_2\text{N-C}_6\text{H}_4\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{O}_2\text{N-C}_6\text{H}_4\text{NH}_3^+ + \text{H}_2\text{O} \]

pKa's: \( \text{CH}_3\text{CO}_2\text{H} = 4.7, \text{CH}_3\text{NH}_2 = 36, \text{CH}_3^+\text{NH}_3 = 10.6, \text{CH}_3\text{CH}_2\text{OH} = 15, \text{H}_2\text{O} = 15.5, \text{HCl} = 7, \text{CH}_3\text{CH}_2\text{OH}^+ = -2, \text{H}_2\text{CO}_3 = 7, \text{NH}_3 = 36, \text{NH}_4^+ = 9.4, \text{H}_3\text{O}^+ = -1.5, \text{PhNH}_3^+ = 4.5, \text{pNO}_2\text{PhNH}_3^+ = 1.0. \)

Based upon the pKa values above, answer the following questions about the following molecule.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{K} \\
\text{C} \\
\text{K} \\
\text{C} \\
\text{O}
\end{array}
\]

\[\text{pK}_a = 5 \quad \text{pK}_a = 23\]

Circle the bases that will completely remove one of each of the indicated protons.

\( \text{NH}_2 \quad \text{H}_2\text{O} \quad \text{HCO}_3 \quad \text{OH} \)

Circle the bases that will remove only the proton from the most acidic position.

\( \text{NH}_2 \quad \text{H}_2\text{O} \quad \text{HCO}_3 \quad \text{OH} \)

Treatment of this molecule with \(-\text{OCH}_3\) will remove protons of:

\[\text{pK}_a = 5 \quad \text{pK}_a = 23 \quad \text{both} \quad \text{neither}\]