1. Rank the following set in order of increasing basicity (least basic first, most basic last):
   Aniline (A), p-cyananiline (B) and p-methoxyaniline (C)
   \[ \text{Rank: } C \rightarrow A \rightarrow B \]

2. Rank the following set in order of increasing acidity:
   Benzoic acid (A), p-nitrobenzoic acid (B), and p-amino-benzoic acid (C)
   \[ \text{Rank: } C \rightarrow A \rightarrow B \]

3. Could you prepare hexanamine (N-hexylenamine) by:
   a. treating 1-bromohexane with cyanide ion (CN\(^{-}\)) followed by reducing the corresponding nitrile so formed with LAH (LiAlH\(_4\)),
   b. treating 1-bromohexane with azide ion (N\(_3\)) followed by reducing the alkyl azide so formed with LAH,
   c. either reaction listed above
   d. neither reaction listed above.

Write the equation(s) for the reaction(s) you chose.

\[ C-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{CH}_3 \xrightarrow{\text{N}_3^-} C-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{N}_3 \]

4. Prepare the compound A listed below starting with benzene and any organic and inorganic reagents. Possible reactions you might need are: nitration, halogenation, reduction, acylation, diazotization, alkylation, acylation, oxidation.
   IMPORTANT, you will not have to use all these reactions, only those that get you to the target molecule. I am just being helpful.
Problem 4a - NOMENCLATURE

Name the following compounds using common names of IUPAC names:

- 2-n-Pentyl formate
- 2-n-Pentyl methanethiosulfonate
- 3-Amino glutaric acid
- N,N-Dimethyl 3-nitro alanine
- γ-Propiolactone
- 3-Aminopropanoic acid lactam
- 5-Hydroxy-2-methylpentyl lactone
- 4-Hydroxy pentanoic acid lactone
5. Consider compound B shown below.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{H} \\
\text{Me} & \quad \text{Me} \\
\text{CH(Me)}_2 & \quad \text{El} \\
& \quad \text{Me} \\
\text{N} & \quad \text{N}
\end{align*}
\]

Me = methyl

a. Write the 3-D structure of the major alkene formed when compound B is treated with MCPBA (delivers an oxygen atom to the nitrogen atom) then heated gently. Skeleton alkene is given below, free of charge.

\[
\begin{align*}
\text{H} & \quad \text{CH} \quad \text{CH} \\
& \quad \text{Me} \quad \text{Cl}
\end{align*}
\]

b. Write the 3-D structure of major alkene formed when compound B is exhaustively methylated with CHJ and then treated with AgO and heated vigorously.

\[
\begin{align*}
\text{H} & \quad \text{CH} \quad \text{CH} \\
& \quad \text{Me} \quad \text{Cl}
\end{align*}
\]

6. Give the mechanism for the acid catalyzed Fisher esterification of benzoic acid (PhCO₂H) and Me³OH. You must show clearly which product (i.e. ester or water) contains the H²O isotope. PLEASE do each step in logical fashion – don’t combined two or more steps in you mechanism.

\[
\begin{align*}
\text{Ph} & \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \quad + \quad \text{H}^+ \quad \rightarrow \quad \text{Ph} \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \\
\text{Ph} & \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \quad \quad \text{+} \quad \text{H}^+ \quad \rightarrow \quad \text{Ph} \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \\
\text{Ph} & \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \quad \quad \text{+} \quad \text{H}^+ \quad \rightarrow \quad \text{Ph} \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \\
\text{Ph} & \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}} \quad \quad \text{+} \quad \text{H}^+ \quad \rightarrow \quad \text{Ph} \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{O}}{\text{H}}
\end{align*}
\]
7. Carry out the following reactions:

a. PhBr
   1. Mg/ Et_2O
   2. CO_2
   3. acidic workup

b. PhCH_2CO_2H
   1. LAH
   2. acidic workup

   CH_2=CHCO_2H

   SOCl_2

   C_4H_7CO_2H

   MeNH_2

   CH_2=CHCO_2H

   C_4H_8O_2

d. PhCH_2OH

   O

   PhCH_2OH

   C_4H_8O_3H

   O

e. HOH

   heat

   NH_2

   O

   HC

   MeH

   N

   4

f. CH_3CH_2CHO

   ON/NaOH

   self Aldol

   CH_2=CHCHO

   OH

   CH_2=CHCHO

   2H

3

3

4

6

4

6

24
8. List the following in order of decreasing reactivity in nucleophilic acyl substitution reactions.

Acetamide (A), propionyl chloride (B), ethyl propionate (C), and acetic acid anhydride (D)

\[ B > D > C > A \]

9. Consider the acid catalyzed acylation of benzene using acetic acid anhydride and AlCl₃.
   a. What is the electrophile that adds to acetic acid anhydride (first step of mechanism)?

   b. To which oxygen atom does the electrophile add? (C=O or C-O)

   c. What are the resulting charges on the oxygen atom and atom of the electrophile attached to the oxygen atom?

   d. What is the nucleophile that attacks the adduct formed in c above?

10. Give the aldol or Claisen product for the following.

   a. [Diagram of aldol reaction with products]

   b. \( \text{CH}_3\text{CH}_2\text{COMe} + \text{MeOOCMe} \rightarrow \text{OMe} \)

   c. [Diagram of Claisen reaction with products]

   d. [Diagram of aldol reaction with products]
11. Deduce the starting ester, ketone or aldehyde for the following cyclic compound.

12. Which of the following can be prepared in good yield by a Claisen or Aldol condensation reaction. Show work for credit.

13. BONUS Give the mechanism, all steps for the self condensation of ethyl acetate and explain how the use of sodium ethoxide drives the equilibrium to completion even though the first step is decidedly in favor the starting ester.
\[
\begin{align*}
\text{Fe}^3+ - O&: C\text{-CH}_2 + \text{NH}_3 \overset{k_1}{\rightleftharpoons} \text{Fe}^2+ - O&: C\text{-CH}_2 - \text{NH}_2 & \text{\(k_1\)} \\
\text{Fe}^3+ - O&: C\text{-CH}_2 \overset{k_2}{\rightarrow} \text{Fe}^2+ - O&: C\text{-CH}_2 \text{O} & \text{\(k_2\)} \\
\text{Fe}^3+ - O&: C\text{-CH}_2 \rightarrow \text{Fe}^2+ - O&: C\text{-CH}_3 & \text{\(k_{\text{obs}} = 10^{-10}\)} \\
\text{Fe}^3+ - O&: C\text{-CH}_2 \rightarrow \text{Fe}^2+ - O&: C\text{-CH}_3 & \text{\(k_{\text{obs}} = 10^{-10}\)} \\
\end{align*}
\]

Reversible