

## AMINES

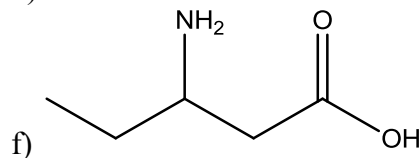
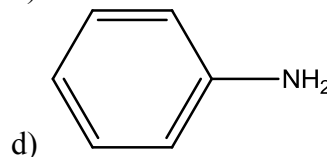
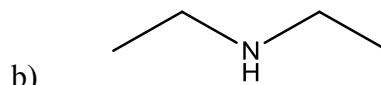
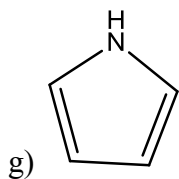
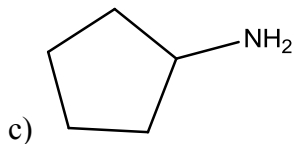
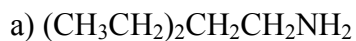
A STUDENT SHOULD BE ABLE TO:

1. Name given the structure, and draw the structure given the name of amines and common nitrogen heterocycles (pyrrole and pyridine). Also, give the classification of compounds in any of the following groups, and give examples of 1<sup>o</sup>, 2<sup>o</sup>, and 3<sup>o</sup> amines and quaternary ammonium salts.
2. Predict the product(s) of reactions giving rise to amines and the reactions of amines, when given the starting materials and reaction conditions. Important reactions include.
  - Acid-base reactions
  - Nucleophilic substitution (including the Gabriel synthesis)
  - Reduction of nitro compounds, azides, amides, and nitriles
  - Reductive amination
  - Reaction of amines and acid chlorides
  - Hofmann Elimination
  - Electrophilic Aromatic Substitution (EAS) reactions of nitrogen heterocycles
3. From your knowledge of the effects involved, predict or explain experimental results. Important areas include:
  - Physical properties (boiling point, solubility)
  - Relative acidity and basicity
  - Nucleophilic substitution (primarily S<sub>N</sub>2)
  - Comparative reactivities
4. Use the reactions of #2 above, plus others learned earlier, to propose syntheses of amines, ammonium salts, and related compounds.
5. Understand and be able to draw the mechanism of acid-base reactions, nucleophilic substitution and elimination reactions. The mechanisms will include all intermediates and proper mechanistic arrows.
6. Predict and interpret IR and NMR spectra and solubility test results to identify unknown amines. Remember that amines, unlike any other common family of organic compounds, are basic.

To best prepare for this module, please work Chapter 23 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Provide names for the following materials.



1.2 Draw the structure of each of the following.

a) diisopropylamine

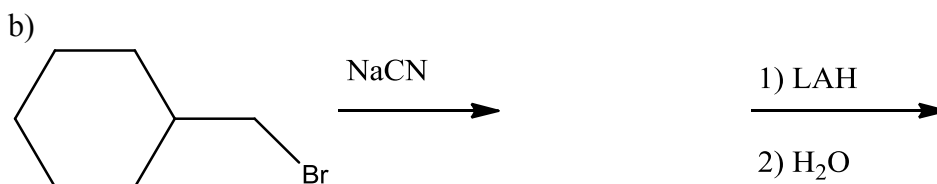
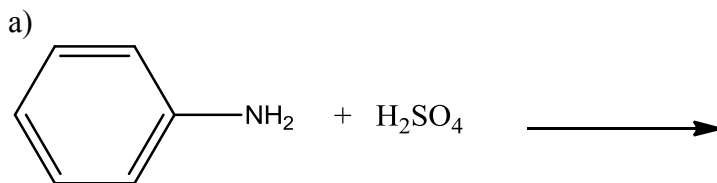
b) 3-amino-1-butanol

c) *para*-bromoaniline

d) (R)-*N*-methyl-*N*-propyl-2-pentanamine

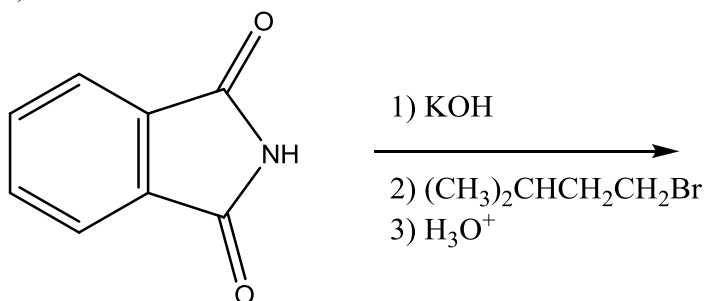
e) 2-methylpyrrole

2. Predict the product or products of the reactions shown (if any)

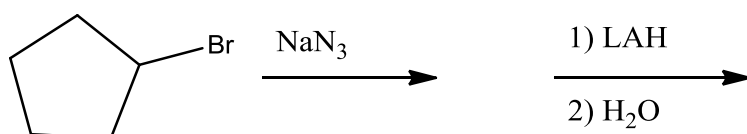


2. (continued)

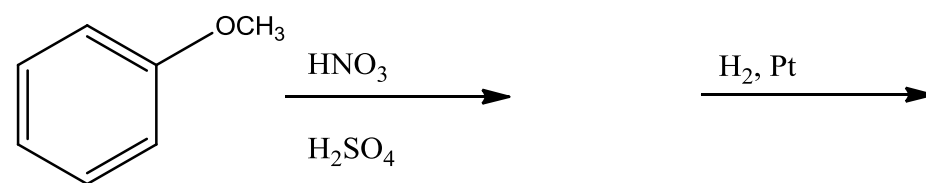
c)



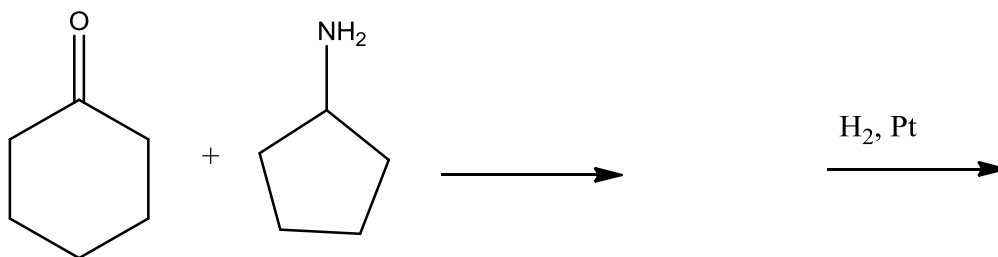
d)



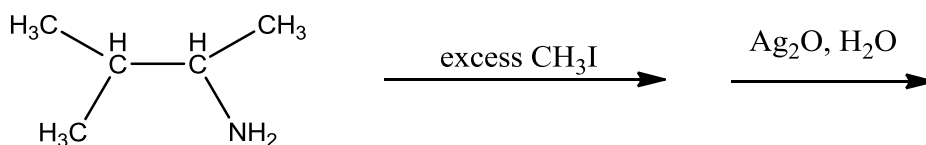
e)



g)

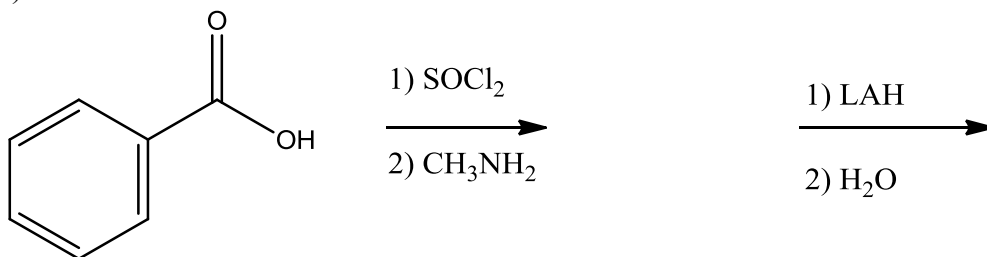


h)

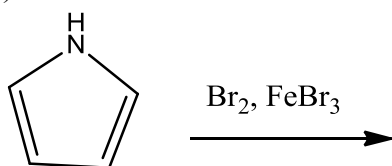


2. (continued)

i)

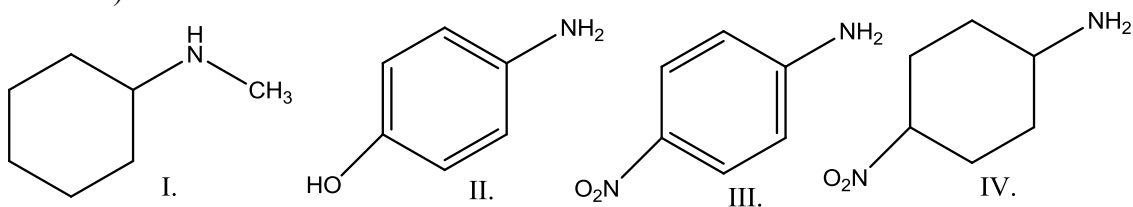


j)



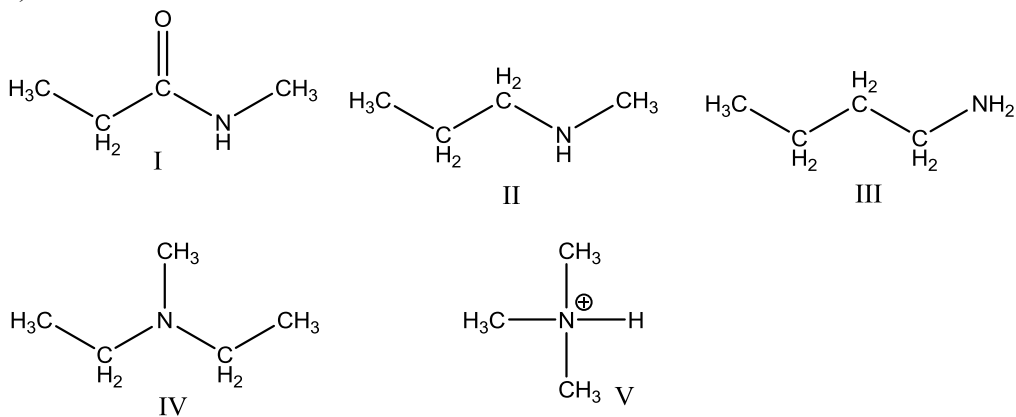
3. 1 Rank the following in terms of most to least basic. (Highest basicity on the left.) Explain why.

a)



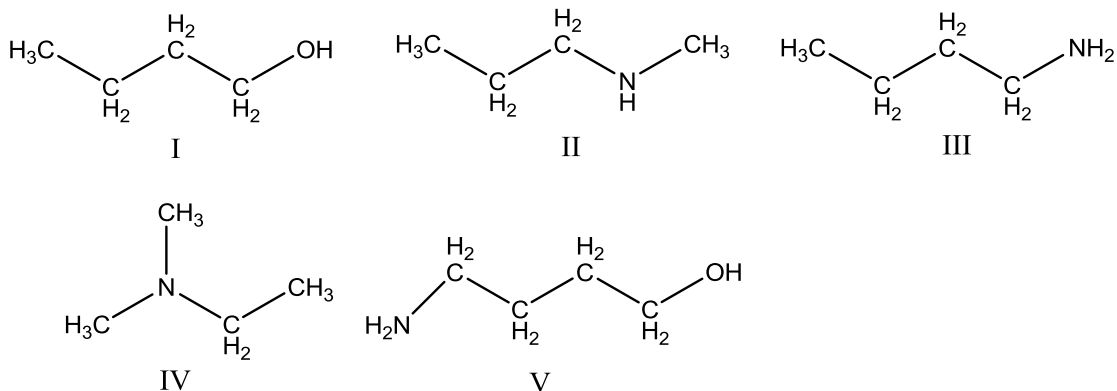
\_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_

b)



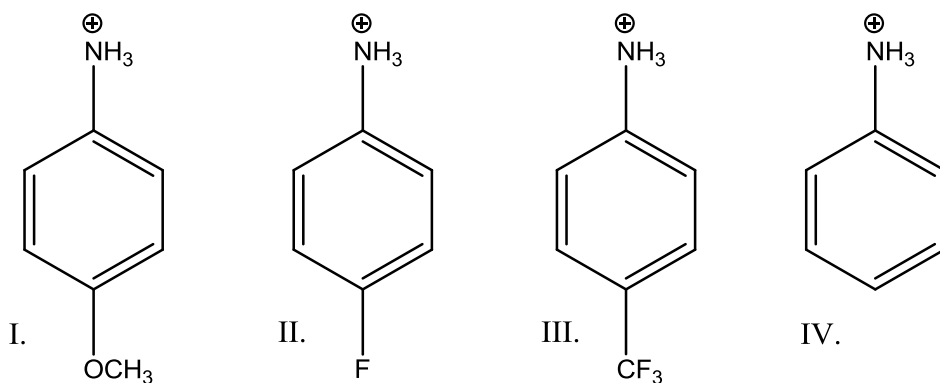
\_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_

3.2 Rank following compounds based on boiling point. (Highest boiling point material on the left.) Explain why.



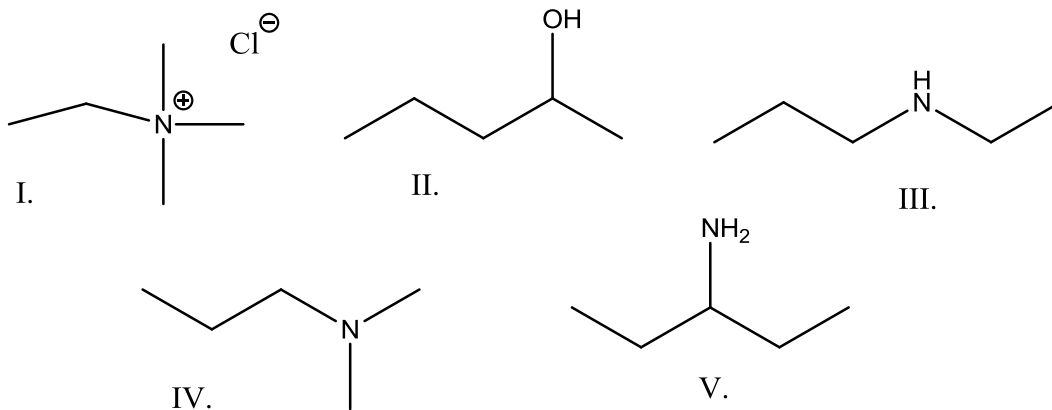
> > > >

3.3 Rank the following in terms of most to least acidic. (Strongest acid on the left.) Explain why.



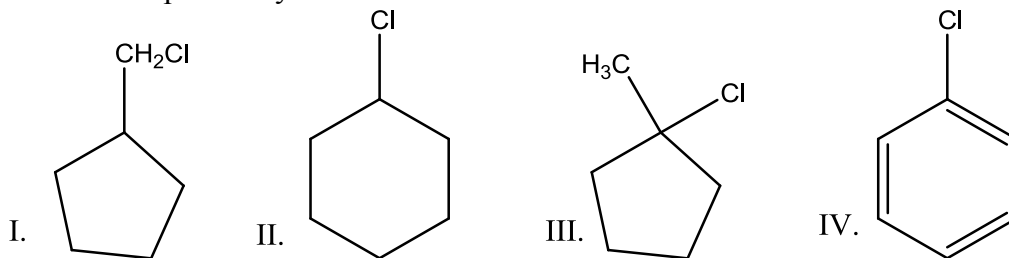
> > >

3.4 Rank the following in terms of most water soluble to least water soluble. (Most soluble on the left.) Explain why.



> > > >

3.5 Which of the following compounds reacts most rapidly with the  $\text{N}_3^-$  ion in an  $\text{S}_{\text{N}}2$  reaction? Explain why.



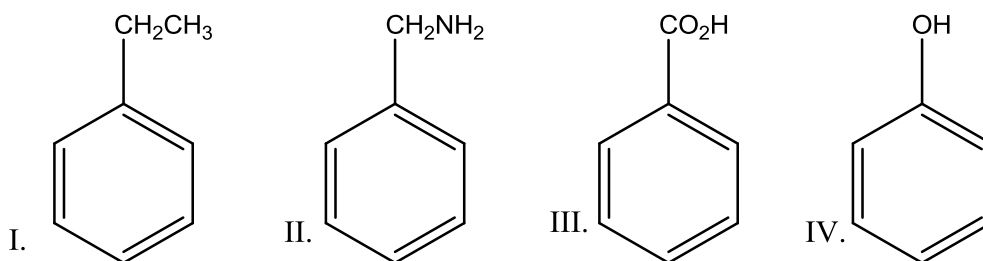
3.6 For these questions, choose the answers from the list of possible compounds at the end of the section.

a) Which of the following compounds is soluble in water and produces an aqueous solution that turns red litmus blue.

b) Which of them is insoluble in water and soluble in 5% HCl?

c) Which of them is insoluble in water, HCl (aq), and  $\text{NaHCO}_3$  (aq), but soluble in NaOH (aq)?

The possible answers are:



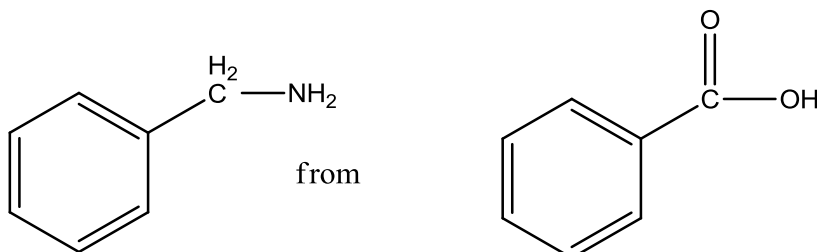
V.  $\text{CH}_3\text{CH}_2\text{NH}_2$

VI.  $\text{CH}_3\text{CH}_2\text{OH}$

VII.  $\text{CH}_3\text{CO}_2\text{H}$

4. Propose a synthesis of each of the following compounds, from the given starting material(s) and any other needed reagents.

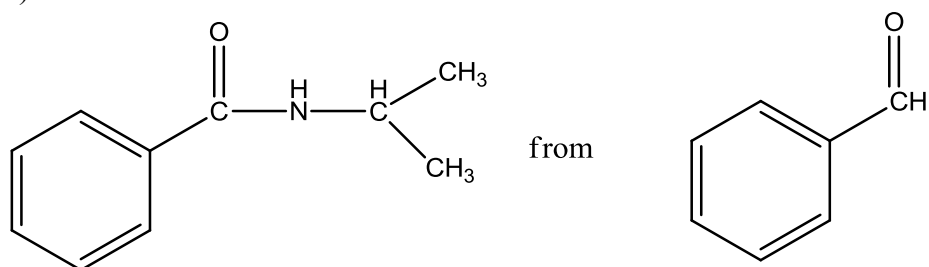
a)



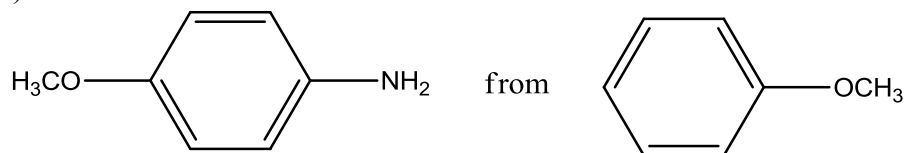
b)  $\text{CH}_3\text{CH}_2\text{NH}_2$  from  $\text{CH}_3\text{CH}_2\text{OH}$

4. (continued)

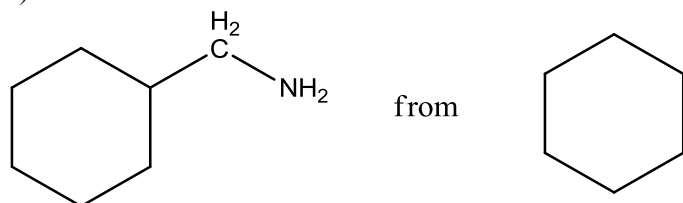
c)



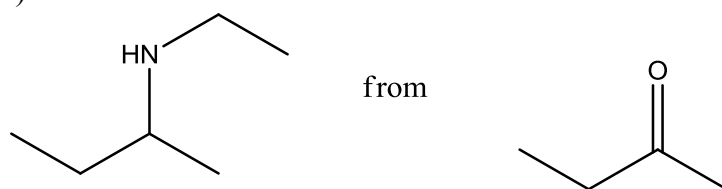
d)



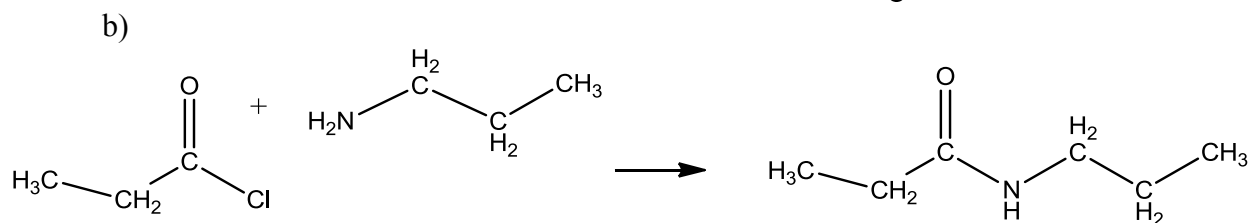
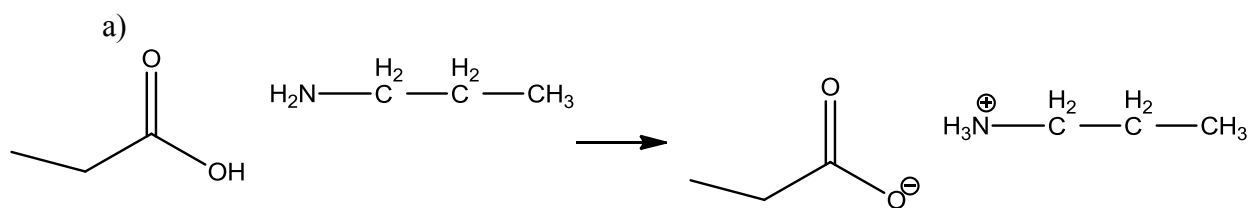
e)



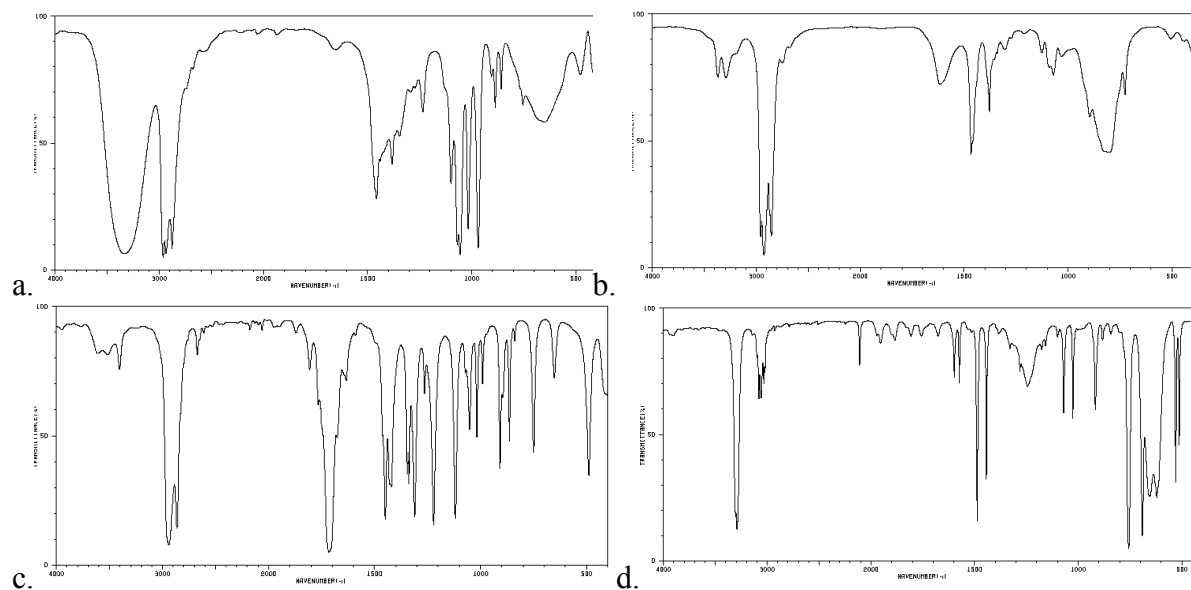
f)



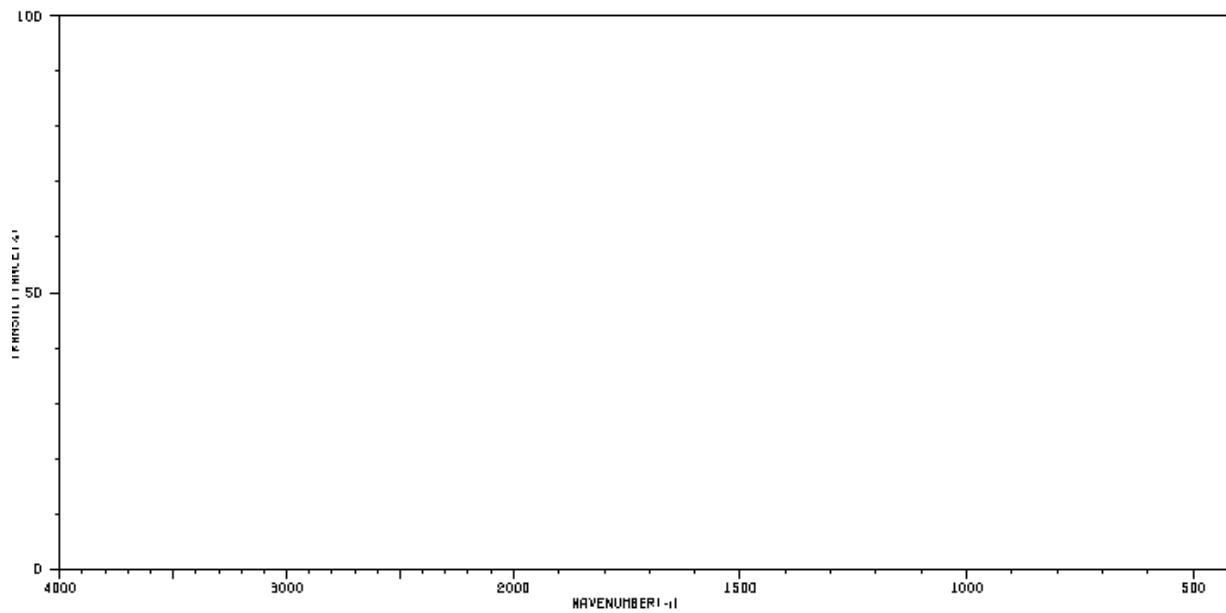
5. Draw the complete mechanism, using proper curved arrow notation, and all intermediates of these reactions.



6.1 Which of these IR spectra belongs to 3-heptanamine?



6.2 Draw what you would expect the IR spectrum to look like for diethylamine.

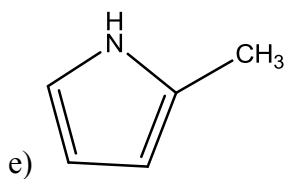
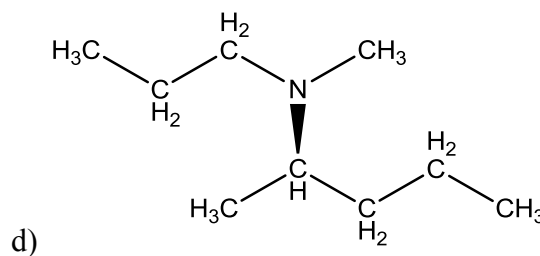
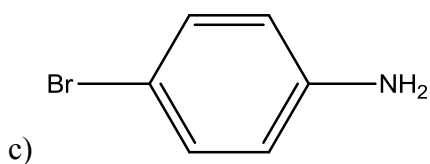
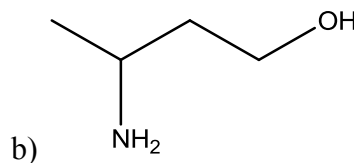
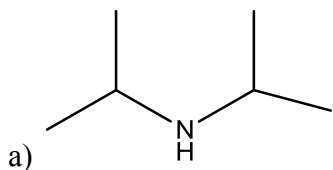


## SOLUTIONS TO SAMPLE PROBLEMS:

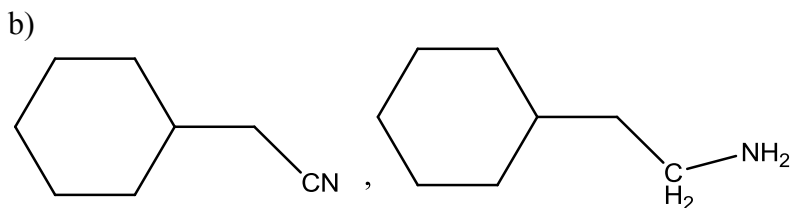
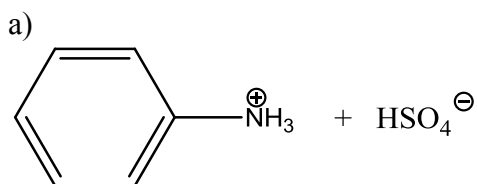
1.1 Provide names for the following materials.

- a) 3-ethyl-1-butanamine
- b) diethylamine
- c) cyclopentyl amine or cyclopentanamine
- d) aniline
- e) 5-chloro-*N*-methyl-1-pentanamine
- f) 3-amino-pentanoic acid
- g) pyrrole

1.2 Draw the structure of each of the following.



2. Predict the product or products of the reactions shown (if any)



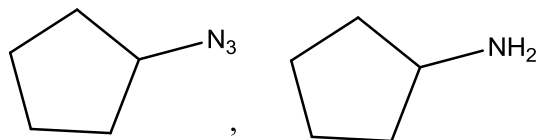
Note the carbon chain was extended by 1.

2. (continued)

c)

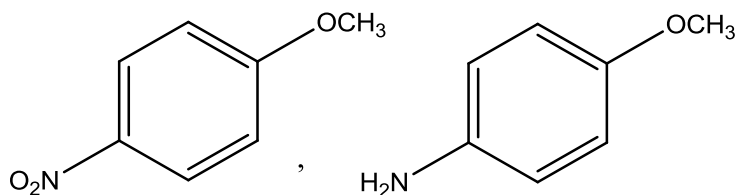


d)

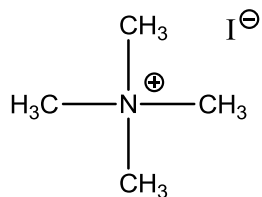


Note same carbon chain length.

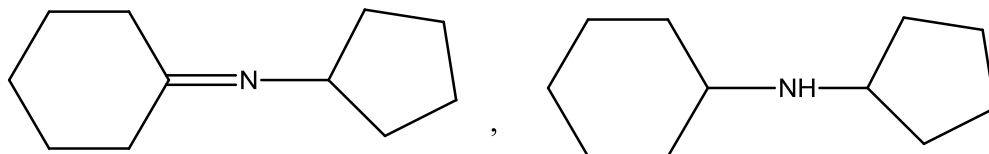
e)



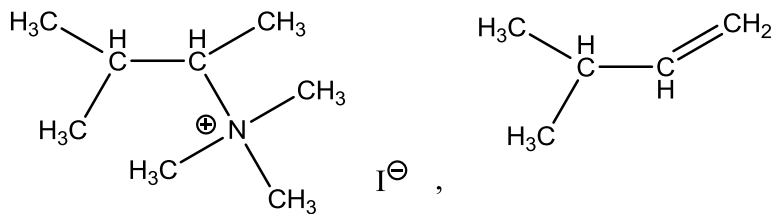
f)



g)



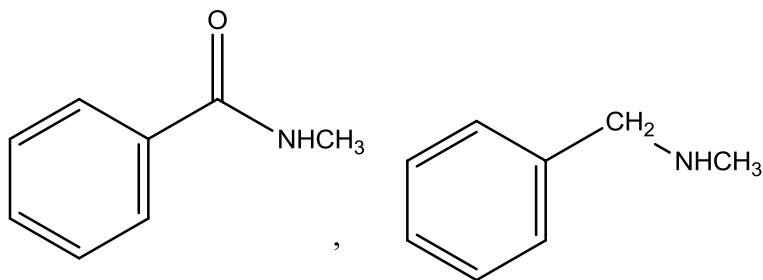
h)



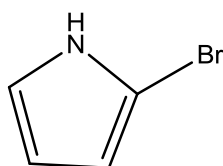
least substituted product.

2. (continued)

i)



j)



3. 1

a) IV > I > II > III

Primary amines are more basic than secondary amines and aryl amines. Secondary amines are more basic than aryl amines. Aryl amines with electron donating groups are more basic than aryl amines with electron withdrawing groups attached.

b) III > II > IV > I > V

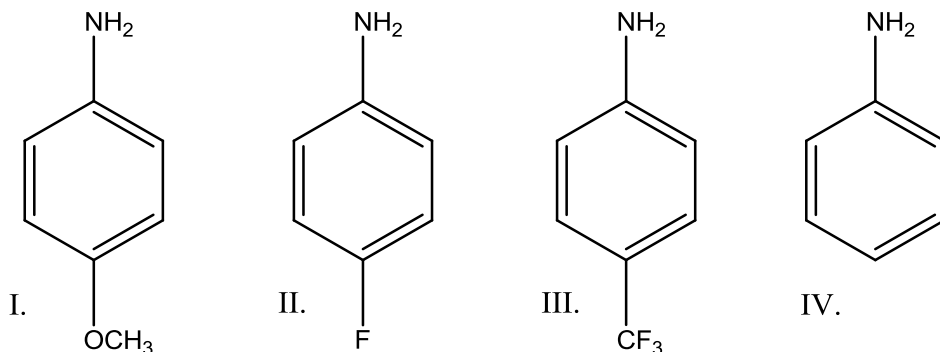
Primary amines are more basic than secondary amines. Secondary amines are more basic than tertiary amines. The quaternary salt will be the least basic because it does not possess any lone electron pairs.

3.2 V > I > III > II > IV

All of the compounds have four carbons. Alcohols have a greater capacity to form hydrogen bonds than amines. Compound V has both an amine and a hydroxyl functional group so it will have the highest boiling point. Primary amines are better able to form hydrogen bonds than secondary amines. Secondary amines are better able to form hydrogen bonds than tertiary amines.

3.3 III > II > IV > I

This may be easier to see if we convert all of the compounds to their conjugate base.



The stronger the base the weaker the conjugate acid. The stronger the base will have the electrons available to participate in hydrogen abstraction. Electron donating groups increase the basicity of aryl amines, hence (I) will be the strongest base and the weakest acid. Trifluoromethyl is a stronger electron withdrawing group than fluorine, hence (III) is the weakest base, and strongest conjugated acid.

3.4 I > II > V > III > IV

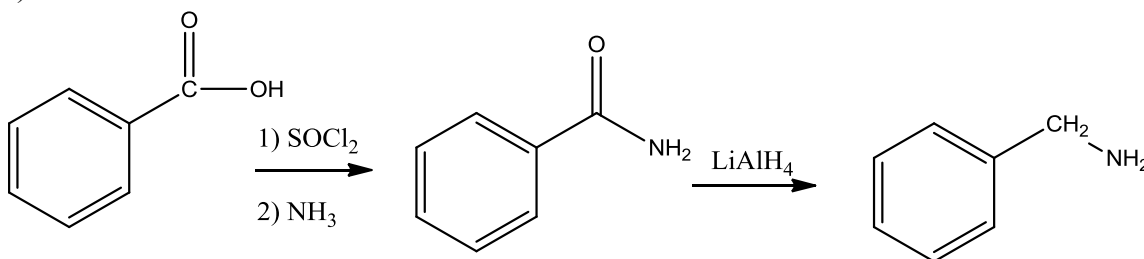
Each compound contains 5 carbons. Ionic materials are the most soluble. Alcohols have a greater capacity to form hydrogen bonds than amines, hence alcohols are more soluble than comparable amines. Primary amines have a higher capacity to form hydrogen bonds than secondary amines. Secondary amines can form more hydrogen bonds than tertiary amines.

3.5  $S_N2$  reactions proceed faster with a primary alkyl halide than a secondary alkyl halide.  $S_N2$  reactions do not occur with aryl halides or tertiary alkyl halides.

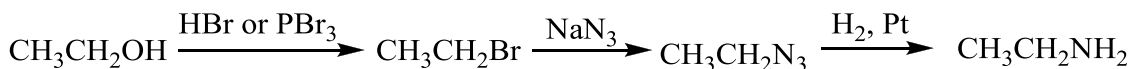
3.6 a) V   b) II   c) IV

4.

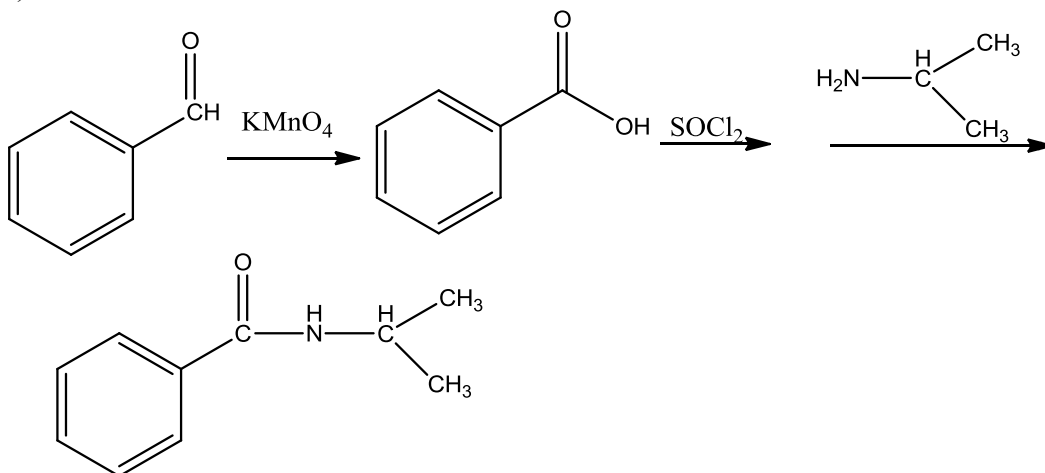
a)



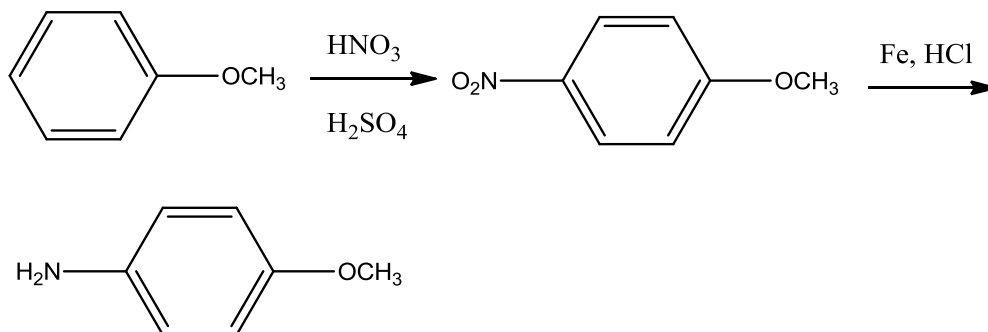
b)



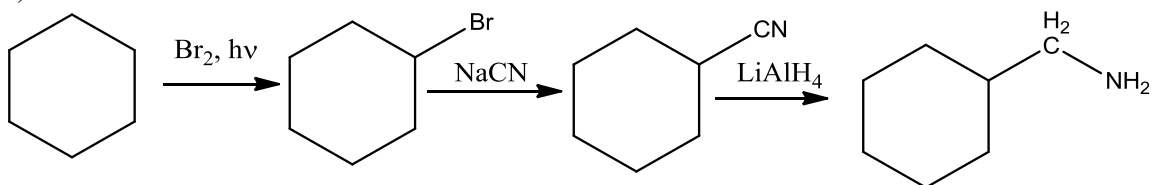
4. (continued)  
c)



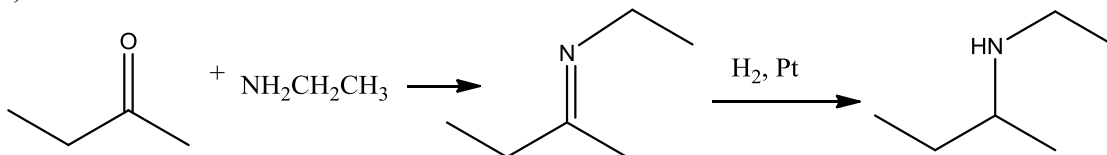
d)



e)

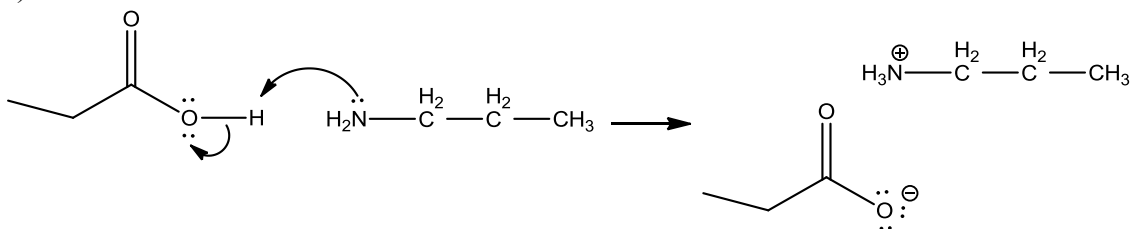


f)

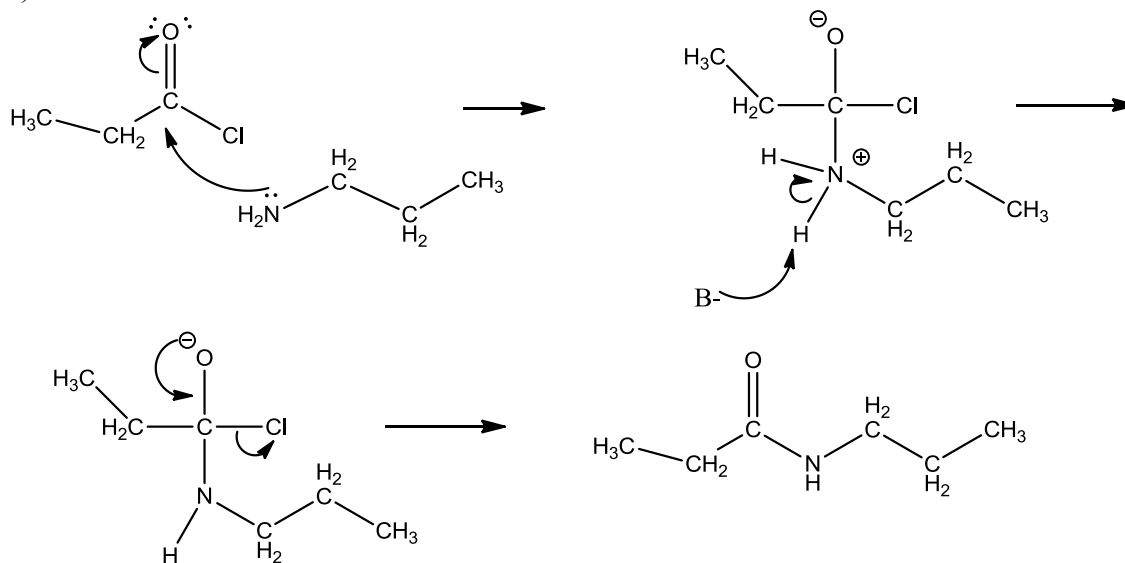


Alternatively can carry out in one step with NH2CH2CH3,  $\text{H}^+$ , NaBH\_3CN.

5. a)

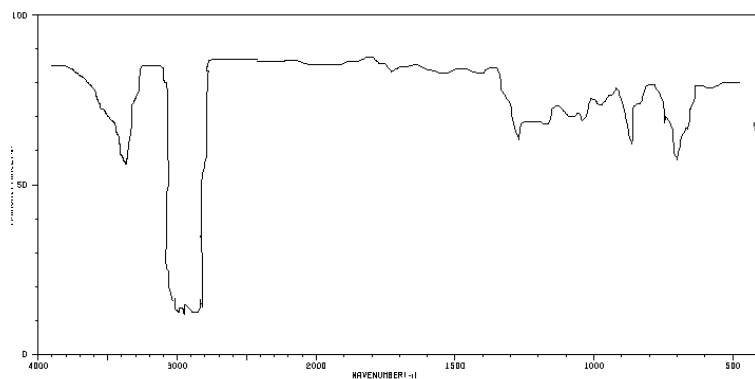


5. b)



6.1 b. Note the characteristic double peaked absorption around  $3400^{-1}$  cm.

6.2 Needs to have a CH absorbance around  $2800-3100\text{cm}^{-1}$  and a secondary N-H absorbance around  $3400\text{cm}^{-1}$ . The NH absorbance should not be as strong as an alcohol, and have a single point.

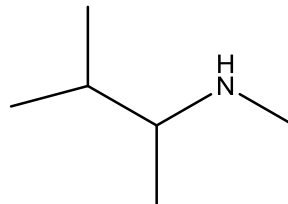


Name \_\_\_\_\_  
Organic Chemistry 2220DR

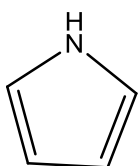
Ninth Drill Test (Sample A)  
Answer All Questions

1. Draw: isobutylamine

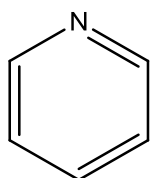
2. Name:



3. Circle the letter which correctly ranks the following compounds according to basicity. (Highest basicity on the left).



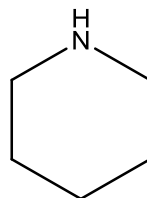
I.



II.



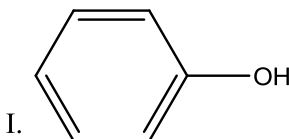
III.



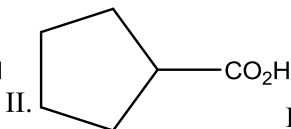
IV.

- a) III > I > IV > II
- b) I > II > IV > III
- c) II > IV > I > III
- d) III > IV > II > I

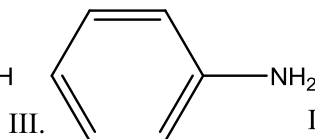
4. Which of the following is insoluble in water and 5 % aq. NaOH, but soluble in 5 % aq. HCl?



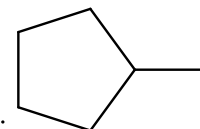
I.



II.



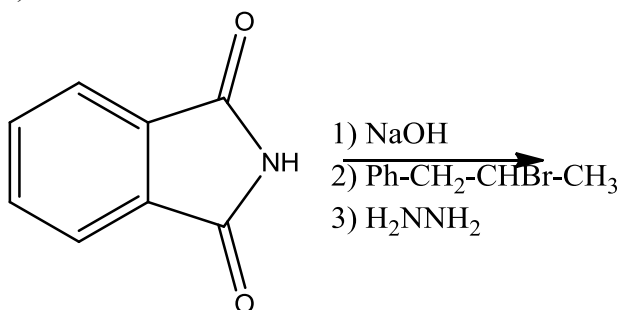
III.



IV.

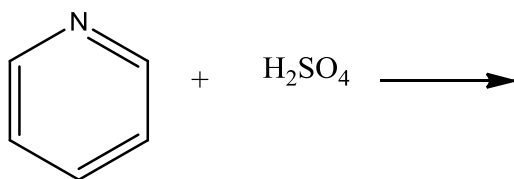
5. Predict the product of each of the following reactions. If no reaction occurs write "N.R."

a)

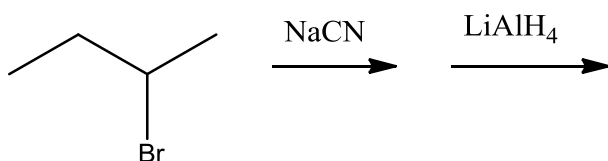


5. (continued)

b)

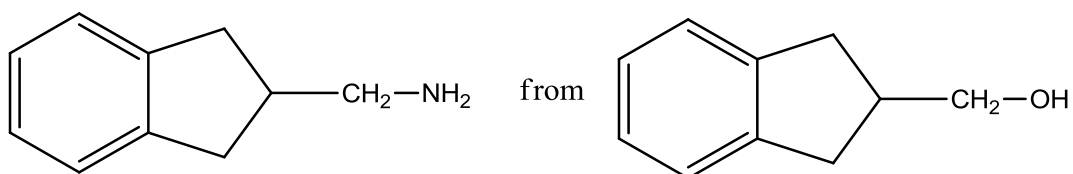


c)

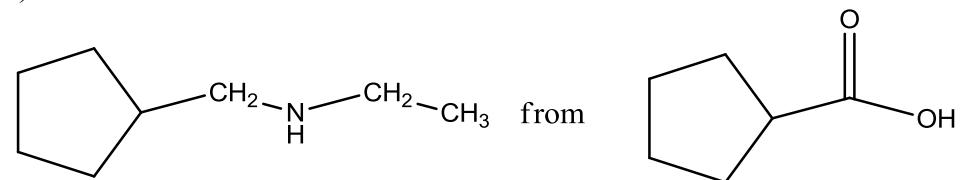


6. Propose a synthesis of each, from the given starting material and any other needed reagents.

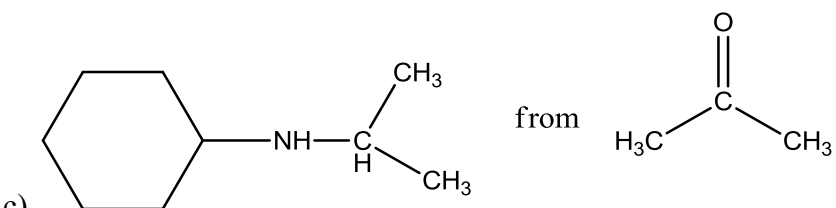
a)



b)



c)

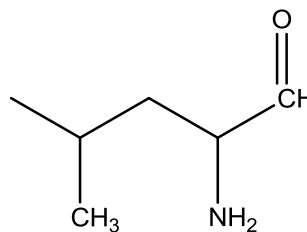


Name \_\_\_\_\_  
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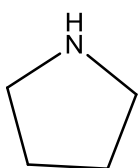
Ninth Drill Test (Sample B)  
Answer All Questions

1. Draw: (S)-N,N-dimethyl-2-hexanamine

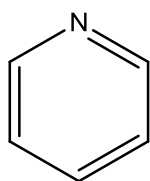
2. Name:



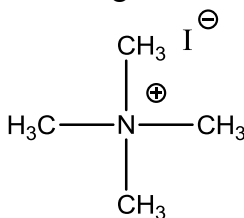
2. Rank the following compounds according to basicity. (Highest basicity on the left).



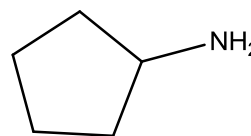
I.



II.



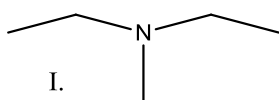
III.



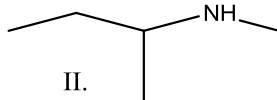
IV.

- a) IV > I > II > III
- b) IV > III > I > II
- c) I > IV > II > III
- d) III > IV > I > II

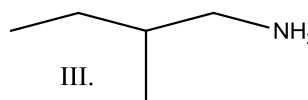
3. Which of the following is MOST soluble in water?



I.



II.

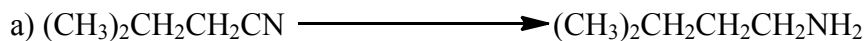


III.

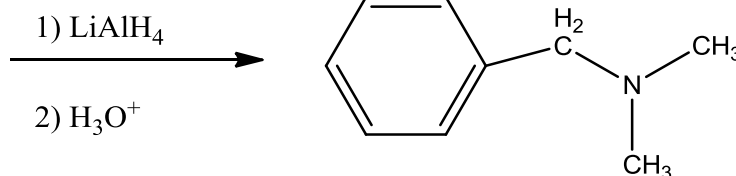


IV.

4. Complete the following reactions.

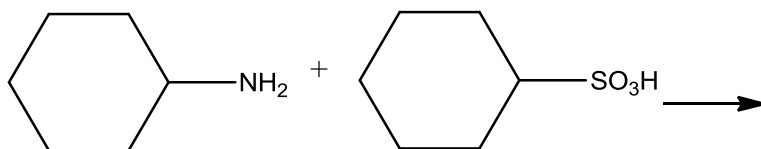


b)

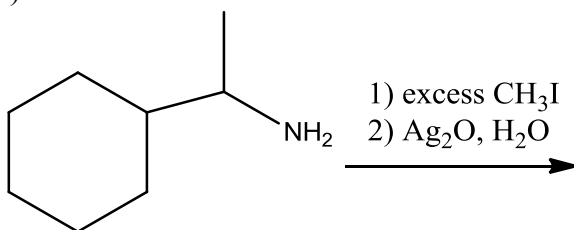


4. (continued)

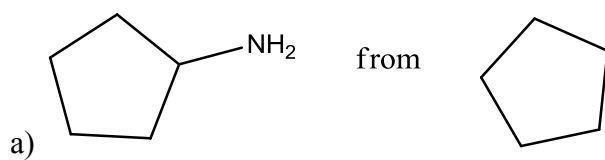
c)



d)



5. Propose a synthesis of each, from the given starting material and any other needed reagents.



b) pentylamine from pentanoic acid