

***Please read the following before proceeding***

1. The exam is divided into these parts.

**Part A is Scantron scored (with extra credit, 44 points)**

- a. Bubble-in your GTID number correctly.
- b. Bubble-in the TEST FORM, located at the top of the page.

**Parts B & C are free response (60 points)**

**Exam 4 total (104 points available)**

2. Materials: Turn off cell phones and wireless PDA devices. Place all other materials on the floor. You will only need a pencil. Molecular models are optional.
2. Show your Buzz Card when you turn in your completed exam.
3. You must work alone.
4. This is a closed book exam. Give or take no assistance from other students. Recall the Georgia Tech Honor Code.

“I pledge my honor that I have not violated the Honor Code during this examination.”

Signed \_\_\_\_\_

PART A – Scantron Scored

(44 points, 4 points each) Bubble-in the correct answer on the Scantron card. There is only one correct answer. Also circle your answer below for later review with the answer key.

1. Which of the following is **not** true about the first tetrahedral intermediate that is formed in the acid-catalyzed hydrolysis of acetamide ( $\text{CH}_3\text{CONH}_2$ )?
  - A) It contains one amino group.
  - B) It contains one OH group.
  - C) It contains one protonated amino group.
  - D) It contains one protonated OH group.
  - E) It contains one methyl group.
  
2. A carboxylic acid derivative will undergo a nucleophilic acyl substitution reaction provided that
  - A) the substituent attached to the acyl group in the reactant is a very strong base.
  - B) the incoming nucleophile and the substituent attached to the acyl group in the reactant have similar basicities.
  - C) the incoming nucleophile is not a much weaker base than the substituent attached to the acyl group in the reactant.
  - D) the incoming nucleophile is not a much larger base than the substituent attached to the acyl group in the reactant.
  - E) the incoming nucleophile is not a much stronger base than the substituent attached to the acyl group in the reactant.
  
3. In an acid-catalyzed reaction all organic reactants, intermediates, and products are
  - A) positively charged
  - B) neutral
  - C) negatively charged
  - D) A and B
  - E) A, B, and C
  
4. What is the leaving group in the acid-catalyzed hydrolysis of acetamide?
  - A)  $\text{H}_3\text{O}^+$  (hydronium ion)
  - B)  $^+\text{NH}_4$  (ammonium ion)
  - C)  $^-\text{NH}_2$  (amide ion)
  - D)  $\text{NH}_3$  (ammonia)
  - E)  $\text{H}_2\text{O}$  (water)

5. An excess of which of the following compounds will optimize the yield of n-propyl acetate ( $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) in an equilibrium mixture of methyl acetate, propyl alcohol, propyl acetate, and methyl alcohol?
  - A) propionic acid
  - B) propyl alcohol**
  - C) methyl alcohol
  - D) acetic acid
  - E) water
  
6. Which of the following reactions would **not** give the indicated product?  
 (acetyl =  $\text{CH}_3\text{CO}$ ; acetate =  $\text{CH}_3\text{CO}_2$ ; benzoate =  $\text{PhCO}_2$ ; benzamide =  $\text{PhCONH}_2$ )
  - A) acetic anhydride + methanol to give methyl acetate + acetic acid
  - B) acetyl chloride + hydroxide to give acetic acid + chloride
  - C) propanamide + methanol to give methyl propanoate + ammonia**
  - D) methylbenzoate + ammonia to give benzamide + methanol
  - E) phenyl acetate + methanol to give methyl acetate + phenol
  
7. Which of the following reactions results in the formation of a carboxylic acid?
  - A) acyl halide +  $\text{H}_2\text{O}$
  - B) nitrile +  $\text{H}_2\text{O}$  (need heat)
  - C) ester +  $\text{H}_2\text{O} + \text{H}^+$
  - D) All of the above
  - E) A and C**
  
8. Which of the following is required to convert propionic anhydride into *N*-methylpropionamide?
  - A) two equivalents of methanol
  - B) one equivalent of methanol
  - C) one-half an equivalent of methylamine
  - D) two equivalents of methylamine**
  - E) two equivalents of ammonia
  
9. Which of the following is the best leaving group?
  - A)  $\text{CH}_3\text{COO}^-$  (acetate ion)
  - B)  $\text{NH}_2^-$  (amide ion)
  - C)  $\text{HO}^-$  (hydroxide ion)
  - D)  $\text{H}_2\text{O}$  (water)**
  - E)  $\text{NH}_3$  (ammonia)

10. Which of the following will result in the formation of a carboxylic acid?

- A) acid-catalyzed hydrolysis of an amide with heat
- B) hydrolysis of an acyl halide
- C) hydroxide ion-promoted hydrolysis of a nitrile with heat
- D) hydrolysis of an acid anhydride
- E) All of the above

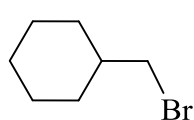
11. Indicate the correct relative acidities (most > least)

- A) a carboxylic acid > protonated water > ammonia > water
- B) protonated water > a carboxylic acid > ammonia > water
- C) protonated water > a carboxylic acid > water > ammonia
- D) ammonia > a carboxylic acid > protonated water > water
- E) protonated water > ammonia > a carboxylic acid > water

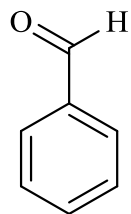
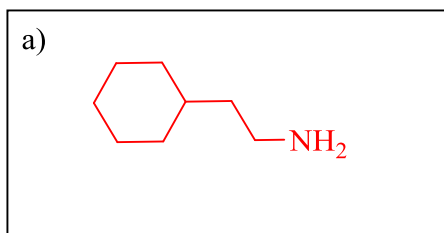
**END of PART A – Scantron scored**

**BEGIN PART B – free response**

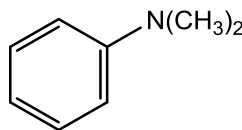
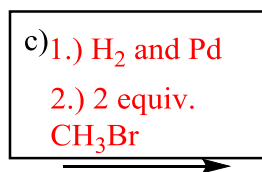
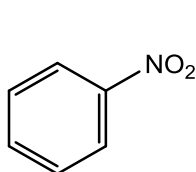
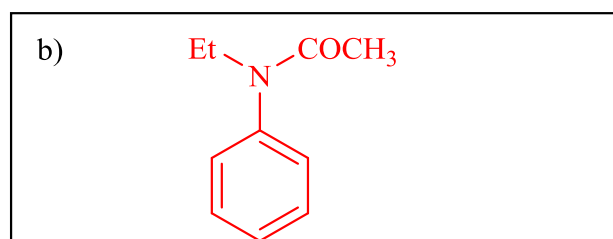
12. (40 points, 4 points each) Provide the structure of the major organic reagent (s) or products(s).



1) NaCN in alcohol  
2) LiAlH<sub>4</sub> in ether  
3) H<sub>2</sub>O and base

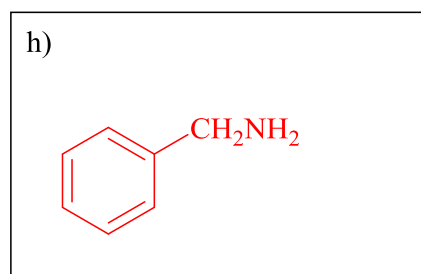
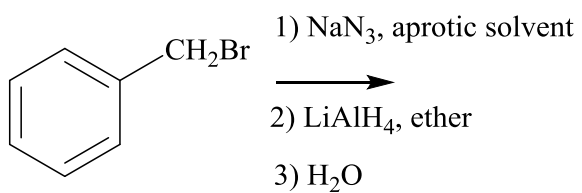
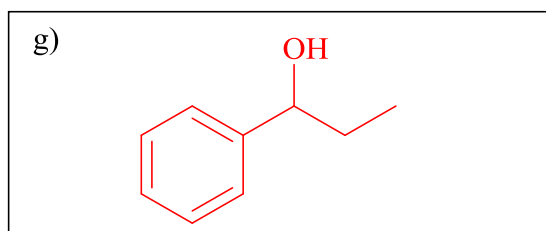
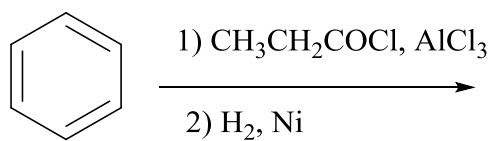
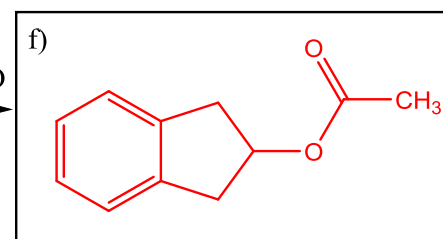
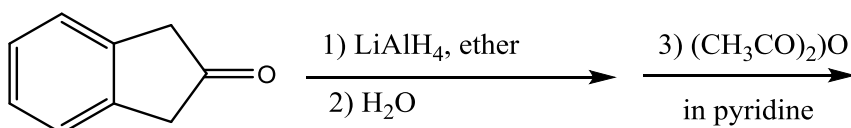
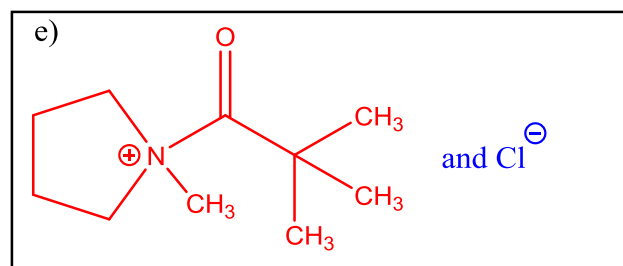
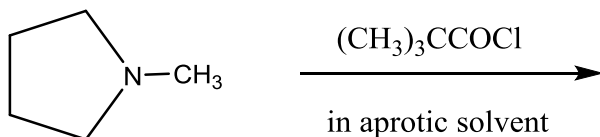
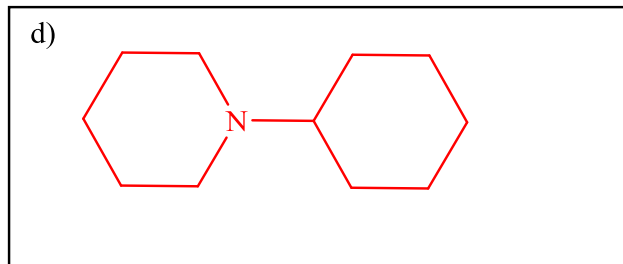
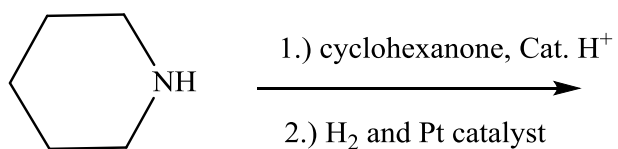


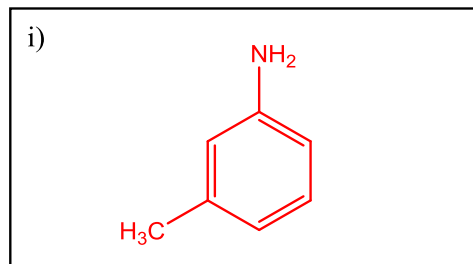
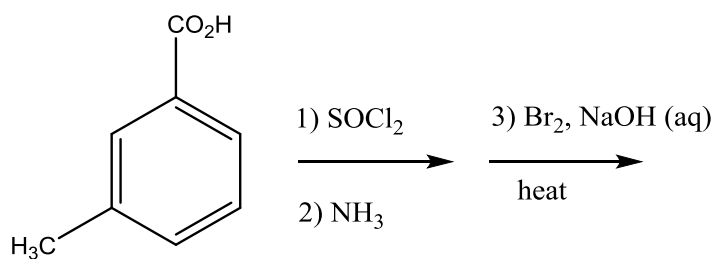
1) EtNH<sub>2</sub>, cat. H<sup>+</sup>  
2) H<sub>2</sub> and Pd cat.  
3) (CH<sub>3</sub>CO)<sub>2</sub>O



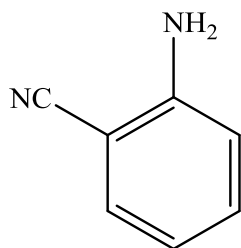
or

- 1.) other reducing agent to convert NO<sub>2</sub> to NH<sub>2</sub>
- 2.) 2 equivalents CH<sub>3</sub>LG LG=leaving group





Would you expect o-cyanoaniline to be a stronger or weaker base than aniline?  
Explain briefly with a drawing or phrase.

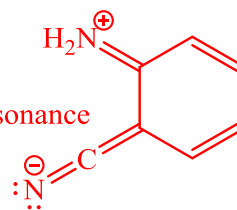


j.)

$\text{pK}_{\text{aH}} = 0.77$  vs aniline 4.58

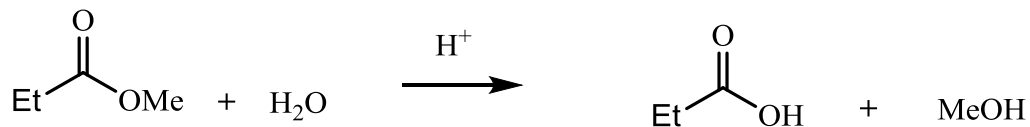
1) Circle one: Stronger or **weaker** than aniline?

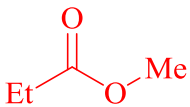
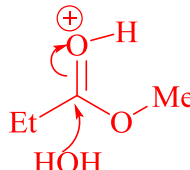
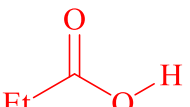
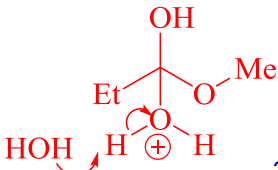
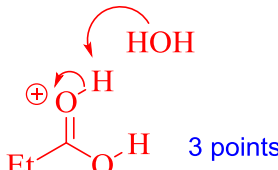
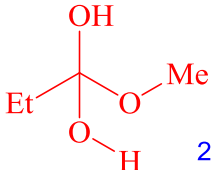
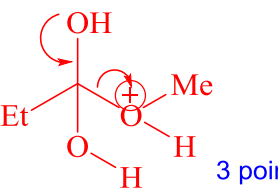
2) Explain: **the lone pair is delocalized via resonance making it a weaker base**

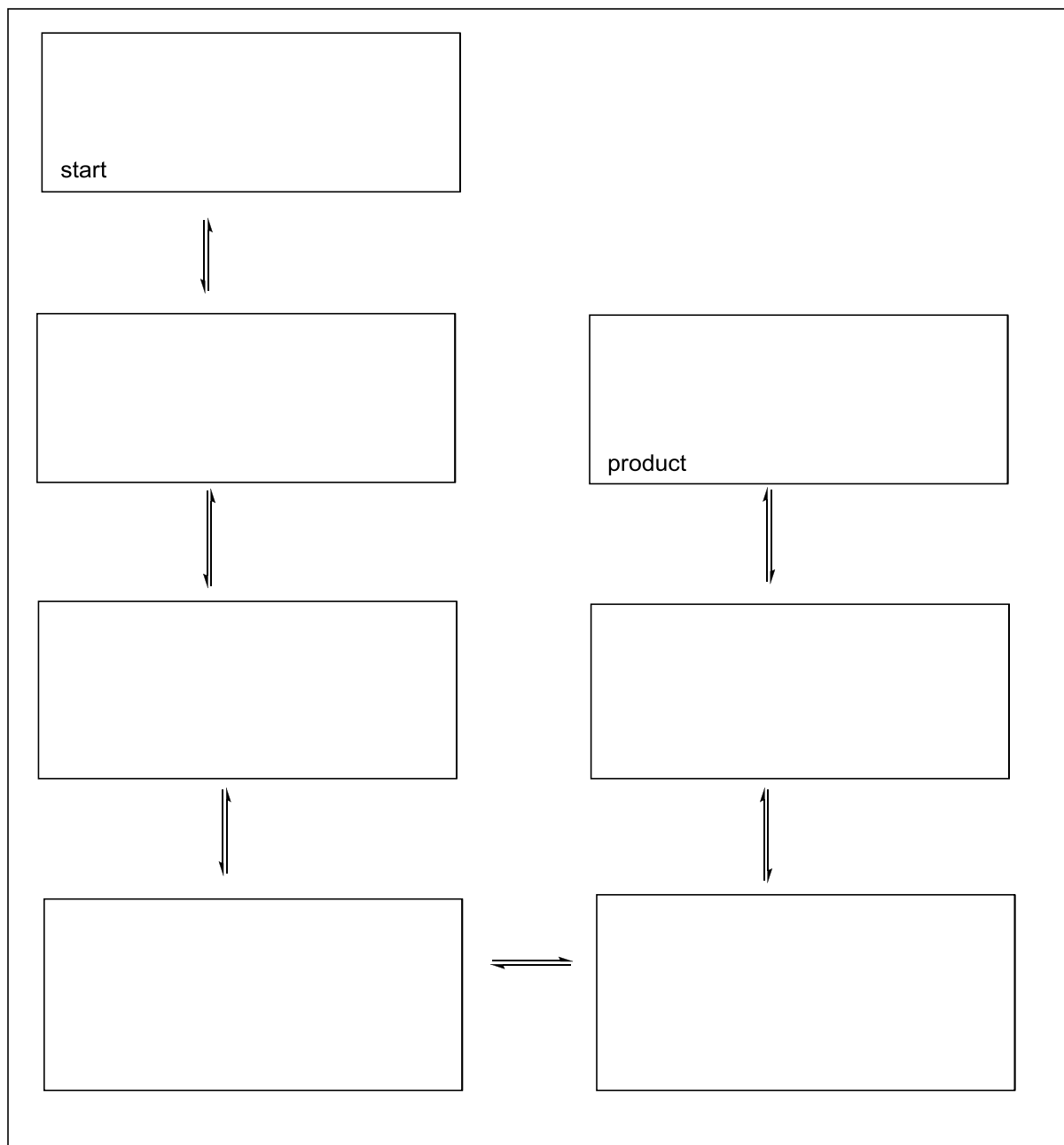


**END PART B**  
**BEGIN PART C**

3. (20 points) Ester hydrolysis is the reaction of an ester with water, which results in the formation of a carboxylic acid. Provide a step-by-step mechanism for the acid catalyzed hydrolysis of methyl propanoate with water to form propionic acid. Water is also the solvent.



<div style="text-align: center;">  <p>start</p> </div>	
<p>Protonation</p> <p>+ H<sup>+</sup> ⇌ 1 point</p>	
<div style="text-align: center;">  <p>3 points</p> </div>	<div style="text-align: center;">  <p>product</p> </div>
<p>Addition</p> <p>+ H<sub>2</sub>O ⇌ 1 point</p>	<p>Deprotonation</p> <p>- H<sup>+</sup> ⇌ 1 point</p>
<div style="text-align: center;">  <p>3 points</p> </div>	<div style="text-align: center;">  <p>3 points</p> </div>
<p>Deprotonation</p> <p>- H<sup>+</sup> ⇌ 1 point</p>	<p>Elimination</p> <p>- MeOH ⇌ 1 point</p>
<div style="text-align: center;">  <p>2 points</p> </div>	<div style="text-align: center;">  <p>3 points</p> </div>
<p>Protonation</p> <p>+ H<sup>+</sup> ⇌ 1 point</p>	



**Answer Key** – *Red are the nominal correct answer expected* – *Blue are further explanation*

**END OF PART C**

**Write your roll number in the box on the next page**

\_\_\_\_\_/ 20



Acid	Approximate $pK_a$	Conjugate Base
$\text{HSbF}_6$	$< -12$	$\text{SbF}_6^-$
$\text{HI}$	$-10$	$\text{I}^-$
$\text{H}_2\text{SO}_4$	$-9$	$\text{HSO}_4^-$
$\text{HBr}$	$-9$	$\text{Br}^-$
$\text{HCl}$	$-7$	$\text{Cl}^-$
$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	$-6.5$	$\text{C}_6\text{H}_5\text{SO}_3^-$
$(\text{CH}_3)_2\text{OH}^+$	$-3.8$	$(\text{CH}_3)_2\text{O}$
$(\text{CH}_3)_2\text{C}=\text{OH}^+$	$-2.9$	$(\text{CH}_3)_2\text{C}=\text{O}$
$\text{CH}_3\text{OH}_2^+$	$-2.5$	$\text{CH}_3\text{OH}$
$\text{H}_3\text{O}^+$	$-1.74$	$\text{H}_2\text{O}$
$\text{HNO}_3$	$-1.4$	$\text{NO}_3^-$
$\text{CF}_3\text{CO}_2\text{H}$	$0.18$	$\text{CF}_3\text{CO}_2^-$
$\text{HF}$	$3.2$	$\text{F}^-$
$\text{CH}_3\text{CO}_2\text{H}$	$4.75$	$\text{CH}_3\text{CO}_2^-$
$\text{H}_2\text{CO}_3$	$6.35$	$\text{HCO}_3^-$
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	$9.0$	$\text{CH}_3\text{COCH}^-\text{COCH}_3$
$\text{NH}_4^+$	$9.2$	$\text{NH}_3$
$\text{C}_6\text{H}_5\text{OH}$	$9.9$	$\text{C}_6\text{H}_5\text{O}^-$
$\text{HCO}_3^-$	$10.2$	$\text{CO}_3^{2-}$
$\text{CH}_3\text{NH}_3^+$	$10.6$	$\text{CH}_3\text{NH}_2$
$\text{H}_2\text{O}$	$15.7$	$\text{OH}^-$
$\text{CH}_3\text{CH}_2\text{OH}$	$16$	$\text{CH}_3\text{CH}_2\text{O}^-$
$(\text{CH}_3)_3\text{COH}$	$18$	$(\text{CH}_3)_3\text{CO}^-$
$\text{CH}_3\text{COCH}_3$	$19.2$	$^-\text{CH}_2\text{COCH}_3$
$\text{HC}\equiv\text{CH}$	$25$	$\text{HC}\equiv\text{C}^-$
$\text{H}_2$	$35$	$\text{H}^-$
$\text{NH}_3$	$38$	$\text{NH}_2^-$
$\text{CH}_2=\text{CH}_2$	$44$	$\text{CH}_2=\text{CH}^-$
$\text{CH}_3\text{CH}_3$	$50$	$\text{CH}_3\text{CH}_2^-$

- ✓ **Write your class roll number on**
  - (a) the top of the first page and
  - (b) in the box to the right.
- ✓ **Verify that you have bubbled in the following on your Scantron card**
  - (a) **Bubbled-In GTID number**
  - (b) **Bubbled-In TEST FORM**

Write your class roll number on (1) the top of the first page and (2) below.

**Class Roll number** \_\_\_\_\_

Part A Scantron scored (44 points)

Page 4 (12) \_\_\_\_\_

Page 5 (20) \_\_\_\_\_

Page 6 (08) \_\_\_\_\_

Page 7 (20) \_\_\_\_\_

Total (Part B&C only) (60) \_\_\_\_\_