Chemistry 1AA3

Test 2

July 22, 2010

McMaster University

VERSION 2

Instructor: P. Hatala

Duration: 120 minutes

This test contains 25 numbered pages printed on both sides. There are 30 multiple-choice questions appearing on pages numbered 3 to 22. Page 24 includes some useful data and equations. There is a periodic table on page 25. You may tear off the last page to view the periodic table and to do your rough work.

You must enter your name and student number on the question sheets, as well as on the answer sheet. Your invigilator will be checking your student card for identification.

You are responsible for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

Questions 1 to 25 are each worth 2 marks, questions 26 - 30 are each worth 3 marks; the total marks available are 65. There is no additional penalty for incorrect answers.

BE SURE TO ENTER THE CORRECT VERSION OF YOUR TEST (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL. Instructions for entering multiple-choice answers are given on page 2.

SELECT <u>ONE AND ONLY ONE</u> ANSWER FOR EACH QUESTION from the answers (A) through (E). No work written on the question sheets will be marked. The question sheets may be collected and reviewed in cases of suspected academic dishonesty.

Academic dishonesty may include, among other actions, communication of any kind (verbal, visual, etc.) between students, sharing of materials between students, copying or looking at other students' work. If you have a problem please ask the invigilator to deal with it for you. Do not make contact with other students directly. Try to keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy.

Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

You are writing VERSION 1 of this test. Make sure you have correctly entered your version number ("1") in the correct column on your scan sheet (see p. 2 for details).

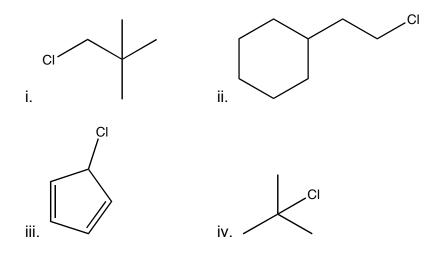
## Section #1 – These questions are worth two marks each.

- 1. Which of the following reagents would best allow you to distinguish between propanone and propanal?
  - a. PCC
  - b. NaBH₄
  - c. potassium permanganate
  - d. HCI
  - e. NaOH

Propanone can't be oxidized while propanal can.

- 2. When considering the reaction between sodium hydroxide and 2-chlorobutane:
  - a. The hydroxide is considered the leaving group
  - Carbon 2 (C2) has a positive dipole because of the chlorine group attached to it
  - c. The product will be a ketone
  - d. The chlorine acts as an electrophile
  - e. The product will be a primary alcohol
    - a. False the hydroxide is the nucleophile
    - b. True
    - c. False product will be an alcohol

3. Which of the following compounds would definitely use an  $S_N2$  mechanism when reacting with an appropriate nucleophile?

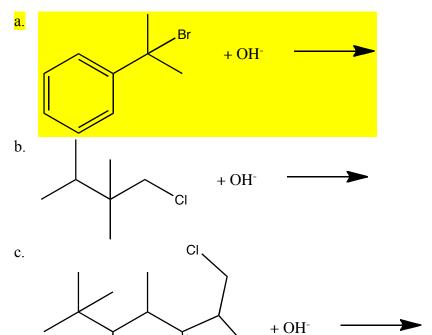


a. ii, iv
b. i, ii
c. i, ii, iii
d. iii, iv
e. ii PART MARK

Need to have a primary electrophile... i and ii are primary electrophile.

3

4. For which of the following reactions would only the concentration of the electrophile change the rate of the reaction?

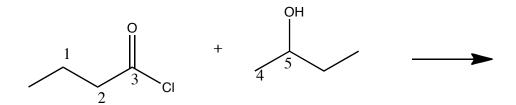


e. All except A.

In order for the concentration of the electrophile to be the sole reactant that determines the rate of reaction, you are looking for an  $S_{\rm N}1$  mechanism. Therefore you need a tertiary electrophile.

4

5. The following reaction first happens via a nucleophilic addition. Based on your knowledge from other reactions that we have studied, on which carbon would you expect the addition to occur and what would be the nucleophile?



- a. C1, the OH group on the alcohol
- b. C4, the Cl group
- c. C2, the OH group on the alcohol
- d. C3, the OH group on the alcohol
- e. C5, the O on the carbonyl

C3 will have a positive charge because of the electron withdrawing from the electron and the chlorine. The OH group will then use it's electrons to form a new bond.

5

6. What would be the following step in this mechanism for the reduction of a ketone using NaBH<sub>4</sub> followed by an acid workup?

a.

<mark>b.</mark>

c.

d.

e.

- 7. Isopropyl alcohol (also known as rubbing alcohol) is reacted with PCC. The product is added to a solution containing an ethyl magnesium chloride followed by an acid workup. The product would be:
  - a. OH

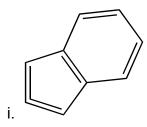
    b. OH

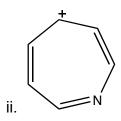
    c. OH
  - e. O

$$\begin{array}{c|c} OH & PCC & \hline \\ \hline \\ H_3O^+ & \hline \end{array}$$

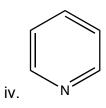
7

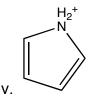
8. Which of the following compounds are aromatic over the entire structure? (you may assumed that they are planar if all other criteria are met)





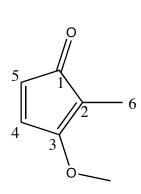


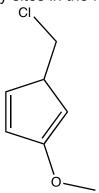


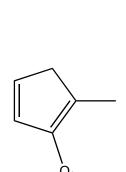


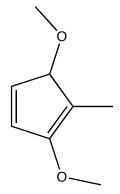
- a. i, iv v
- b. ii, v
- c. iii, iv PART MARK
- d. iv, v
- e. ii, iii, iv

9. Which carbons are diversity sites in the following combinatorial library?









- a. 3, 5, 6
- b. 1, 2
- c. 4, 5
- d. 1, 2, 6
- e. 2, 4, 5

- \_ 10. One of the control tests for the high throughput screening for HVA was a well that had dopamine and HVA only. The test returned a positive result. The purpose of this control is to:
  - a. Ensure that HVA will lower dopamine concentration
  - b. Ensure that HVA is the source of a positive result
  - c. Ensure that neural cells will produce less dopamine when HVA is present
  - d. Ensure that the HVA doesn't interfere with ability of dopamine to register a positive result
  - e. Ensure that dopamine is the source of a positive result
- 11. Which of the following statements about this compound are true?



- i. It is aromatic
- ii. The lone pair electrons on nitrogen are located in the hybridized orbital
- iii. It will remain aromatic upon reacting as a nucleophile
- iv. The length of the C1-C2 bond is equal to the length of the C2-C3 bond
- a. ii, iv
- b. i, iv
- c. i, ii, iv
- d. i, iii, iv
- e. i, ii, iii, iv
  - i. True
  - ii. False lone pair electrons are part of the pi-electron system
  - iii. False it would have to use it's lone pair electrons, rendering it non-aromatic

9

iv. True

12. A 350.0 mL buffer solution is created with final concentrations of 0.250 M HCNO and 0.340 M KCNO. What is the pH of the resulting solution? (pKa HCNO = 3.456)

a. 
$$\frac{3.590}{b. 2.316}$$
b.  $2.316$ 
c.  $8.381$ 
d.  $5.221$ 
e.  $9.374$ 

$$pH = pK_a + \log\left(\frac{A^-}{HA}\right)$$

$$pH = 3.456 + \log\left(\frac{0.340}{0.250}\right)$$

$$pH = 3.590$$

\_\_\_ 13. A solution is created by mixing together:

i. 50.0 mL of 0.350 M HCIii. 25.0 mL of 0.220 M NaOH

iii. 25.0 ML of 0.220 M NaCh

iv. 25.0 mL of 0.500 M HF ( $K_a = 6.3 \times 10^{-4}$ )

v. 20.0 mL of water

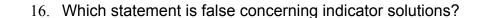
What is the resulting pH?

Before After	HCl + 0.0175 0.012	NaOH $\rightarrow$ NaCl + 5.5x10 <sup>-3</sup> 0 0 5.5x10 <sup>-3</sup>		H <sub>2</sub> O 0 0.0175
NaCl won't	affect the pH.			
Before After	F + 0.012	HCl → 0.012	HF + 0 0 012	C1 <sup>-</sup> 0 0
	After NaCl won't	Before 0.0175 After 0.012  NaCl won't affect the pH.  F + Before 0.012	Before 0.0175 5.5x10 <sup>-3</sup> After 0.012 0 5.5x  NaCl won't affect the pH. $ \begin{array}{cccccccccccccccccccccccccccccccccc$	Before $0.0175$ $5.5 \times 10^{-3}$ $0$ After $0.012$ $0$ $5.5 \times 10^{-3}$ NaCl won't affect the pH. $F^{-} + HCl \rightarrow HF + Before 0.012 0.012 0$

0.0125 mol of HF + 0.012 mol HF = 0.0245 mol/0.15 L [HF] = 0.163 M

- 14. A buffer is created using equal volumes of 0.500 M methanoic acid  $(Ka = 1.8 \times 10^{-4})$  and 0.400 M sodium methanoate. To this buffer, a small amount of 0.200 M potassium hydroxide is added. Select the false statement about this system.
  - a. The volume change associated with this addition is insignificant
  - b. This buffer is most effective between pH ranges of 2.65 and 4.65
  - c. The pH of the system changes because the concentration of methanoic acid decreases
  - d. The system will no longer be a buffer if the concentration of methanoate rises above 0.409 M
  - e. The pH of the system will rise because more methanoate ion will be consumed
    - a. True
    - b. False effective between 2.74 to 4.74
    - c. True
    - d. False
    - e. True
- \_\_\_\_ 15. Select the true statements with respect to the titration of a weak base with a strong acid:
  - i. The pH at  $\frac{1}{2}$  equivalence will equal the  $K_b$  of the base
  - ii. The buffer region will occur between pH 3 5
  - iii. The pH at the equivalence point will be less than 7.0
  - iv. Phenolphthalein (pH range 8.0 10.0) would be an appropriate indicator
  - a. i, iii
  - b. ii, iv
  - c. i, iv
  - d. i
  - <mark>e. iii</mark>
    - i. False ½ equivalance will equal K<sub>a</sub> of conjugate acid
    - ii. False buffer will occur between 8 10
    - iii. True
    - iv. False want something to change in the acid range

11



- a. The common ion effect forces the equilibrium of the indicator to either the acidic or basic form
- b. The indicator should change colour near the equivalence point
- c. An indicator is a weak acid or weak base buffer solution
- d. The  $pK_{IN}$  should be +/- 1 of the  $pK_a$  or  $pK_b$  of the weak acid or base being used
- e. The "acidic colour" represents the indicator in it's protonated form
  - a. True
  - b. True
  - c. True
  - d.  $pK_{IN}$  needs to be +/- 1 the pH of the equivalence point
  - e. True
- \_\_\_\_ 17. A 250.0 mL solution of 0.400M chloroacetic acid (Ka = 1.4 x 10<sup>-3</sup>) is titrated with 0.300 M NaOH. What is the pH at the equivalence point?
  - a. 7.66
  - b. 8.04
  - c. 9.32
  - d. 3.12
  - e. 4.18
- 0.1 mol of acid, therefore need 0.1 mol of base. Add 0.3333 L of solution. At equivalence there will only be the conjugate base (chloroacetate). [chloroacetate] = 0.1715M

	A <sup>-</sup>	+	H <sub>2</sub> O	$\rightleftharpoons$	HA	+	OH-
I	0.1715				0		0
С	-X				+ <b>X</b>		+ <b>X</b>
Е	0.1715-x				X		X

$$K_{b} = \frac{K_{w}}{K_{a}}$$

$$K_{b} = 7.143 \times 10^{12} = \frac{x^{2}}{0.1715 - x}$$

$$x = 1.1068 \times 10^{-6}$$

$$pOH = 5.956$$

$$pH = 8.04$$

- 18. 100.0 mL of water is added to a 0.500 L solution containing 0.250 M ammonium nitrate and 0.200M ammonia. What is the effect of dilution on the pH?
  - a. There is no change in pH
  - b. The acidity decreases by a factor of 2
  - c. The pH of the solution will become neutral
  - d. The pOH will change but not the pH
  - e. None of the above is correct

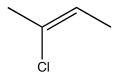
Small amounts of water will keep the ratio of base and conjugate acid the same... won't affect the pH.

- 19. Which of the following would be an appropriate indicator to use for the titration of 100.0 mL of 0.0250 M HNO<sub>3</sub> with 0.0300M LiOH?
  - a. Bromophenol blue (pK = 4.1)
  - b. Metacresol purple (pK = 2.0)
  - c. Methyl red (pK = 5.0)
  - d. Alzarin yellow (pK = 11.2)
  - e. Phenolphthalein (pK = 9.5)

Strong acid with a strong base... will be at pH 7.0 at equivalence. Need an indicator that will change just after the equivalence point (not before)... phenolphthalein is the closest.

20. Which of the following relationships between pairs of molecules are correct?

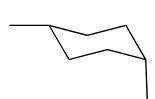
and



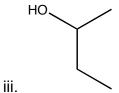
geometric isomers



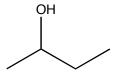
and



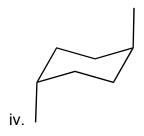
geometric isomers



and



same structure



and



- a. i, iii, iv
- <mark>ii, iii, i∨</mark>
- d. iii
- e. ii, iv
- i. Is an identical item.

21. Indicate the incorrect statement about the compound below:

- a. There are 2 pi-electrons
- b. There is one sp³ hybridized carbon atom
- c. The oxygen is sp<sup>2</sup> hybridized
- d. There are 6 implied hydrogens
- e. The structure is in a E- configuration

Oxygen is sp<sup>3</sup> hybridized

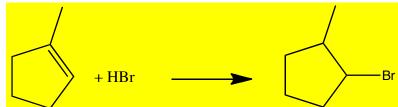
Can't determine E or Z since on the left-hand side there are two hydrogens

22. Which of the following structures do not agree with a Markovinkov addition?

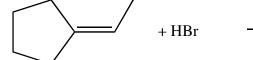
$$+ H_2O$$

b.

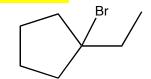
c.



d.



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e. More than two reactions above

- 23. A student attempts the synthesis of aspirin from salicylic acid and runs a TLC on the final product showing both aspirin and salicylic acid in the product. The student can conclude:
  - a. A further recrystallization should provide a pure sample of aspirin
  - b. Some of the aspirin has decomposed back to salicylic acid
  - c. There is a 50:50 mixture of the two compounds
  - d. The melting point should be consistent to that of aspirin
  - e. An IR spectrum on the product will a peak indicative of a carbonyl group
- 24. A student makes three solutions; NaOH, CH<sub>3</sub>COOH and CH<sub>3</sub>COONa. The concentrations are recorded (0.250 M, 0.400 and 0.550), but the student does not remember which concentration is for which solution. When mixing 25 ml of each solution together, the pH is > 10. The student can conclude:
  - a. [NaOH] = 0.250,  $[CH_3COOH] = 0.400$ ,  $[CH_3COONa] = 0.550$
  - b. [NaOH] = 0.550,  $[CH_3COOH] = 0.400$ ,  $[CH_3COONa] = 0.250$
  - c. [NaOH] = 0.400,  $[CH_3COOH] = 0.550$ ,  $[CH_3COONa] = 0.250$
  - d. [NaOH] = 0.550,  $[CH_3COOH] = 0.250$ ,  $[CH_3COONa] = 0.400$
  - e. They could be both b & d

Since the solution is quite basic, you know that the largest concentration must be the sodium hydroxide.

- \_ 25. Equal volumes of LiF and NH₄Cl are mixed together. There pH of the solution would be:
  - a. Not enough information
  - b. Weakly basic
  - c. Highly acidic
  - d. Highly basic
  - e. Weakly acidic

Need to know the concentrations in order to answer this question.

## Section #2 - These questions are worth three marks each.

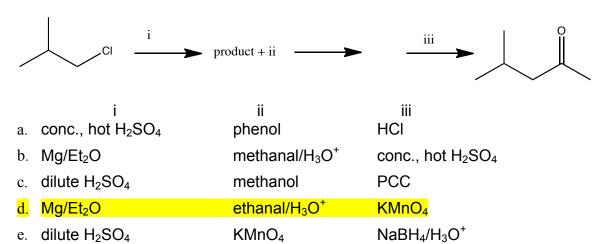
26. Select the true statement based on the following reaction:

$$CH_3CHC(CH_3)CH_2CH_3 + HCI \rightarrow ?$$

- a. The organic compound is the lewis base
- b. The reaction requires a platinum catalyst
- c. The HCl is the nucleophile
- d. The product will be 2-chloro-3-methylpentane
- e. The hydrogen ion is the leaving group

This is the addition of HCl across a double-bond.

27. The catalysts and reactants at i, ii and iii would be:



 $\underline{}$  28. 50.0 mL of 0.350 M CH<sub>3</sub>COOH is mixed with 40.0 mL of 0.250 M Mg(CH<sub>3</sub>COO) <sub>2</sub>. To this solution, 10.0 mL of 0.200 M NaOH is added. What is the resulting pH? ( $K_a$  CH<sub>3</sub>COOH = 1.8 x 10<sup>-5</sup>)

 $Mg(CH_3COO)_2 \rightarrow Mg^{2+} + 2CH_3COO^{-1}$ 

$$pH = pKa + \log\left(\frac{A^{-}}{HA}\right)$$
$$pH = 4.74 + \log\left(\frac{0.22}{0.155}\right)$$
$$pH = 4.90$$

19

- 29. To determine the pKb of a weak base experimentally, one could
  - a. Knowing the pH at the equivalence point in the titration with a strong acid
  - b. Knowing the pH at the half equivalence point in the titration with a strong acid
  - c. Measuring the pH of a known concentration of the weak base
  - d. A, B
  - e. A, B & C

- 30. What mass of solid NaOH must be added to 250.0 mL of 0.350M HN<sub>3</sub> ( $K_a = 2.5 \times 10^{-5}$ ) to make a buffer with a pH of 3.8? Assume no volume change upon the addition of NaOH.
  - a. 1g
  - b. 0.8g
  - c. 0.2g
  - d. 0.5g
  - e. 3g

$$HN_3$$
 + NaOH  $\rightarrow$   $N_3^-$  +  $H_2O$   
Before 0.0875 mol x 0 -----  
After 0.0875 - x 0 x -----

Don't need to convert to concentration because both the weak acid and conjugate base are divided by the same volume.

$$pH = pK_a + \log\left(\frac{A^-}{HA}\right)$$

$$3.8 = 4.6021 + \log\left(\frac{x}{0.0875 - x}\right)$$

$$x = 0.011922mol$$

$$0.011922 mol \left( \frac{39.9969 g}{1 mol} \right)$$
  
= 0.5 g