UNIVERISTY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING
CHE 391s Organic Chemistry and Biochemistry
Final Exam - Tuesday April 20th, 1999
EXAMINER: Prof. E.A. Edwards

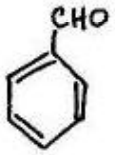
Answer all questions in the spaces provided. (14 pages; 22 questions)

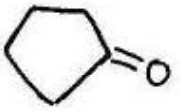
Name_____ Student Number:_____

Marks or Minutes	Questions:

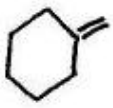
1. Predict the products of the reactions (briefly justify your answer and name reaction type or mechanism):

2 a) $CH_3CHBrCH_2CH_3 \xrightarrow{base}$

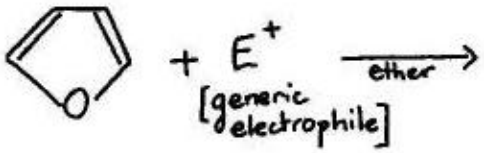
2 b)  $+ Cl_2 \longrightarrow$

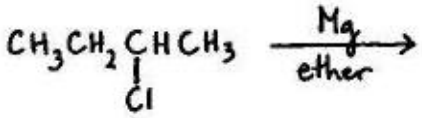
2 c)  $\xrightarrow[2.\ H_3O^+]{1.\ NaBH_4}$

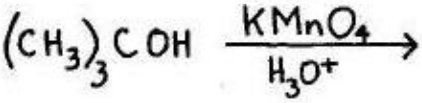
2 d) $CH_3CH_2OH + CH_3CH_2COOH \xrightarrow{H^+}$

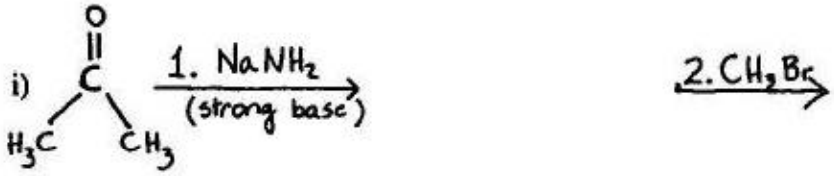
2 e)  $+ H_2O \xrightarrow[\Delta]{H^+}$

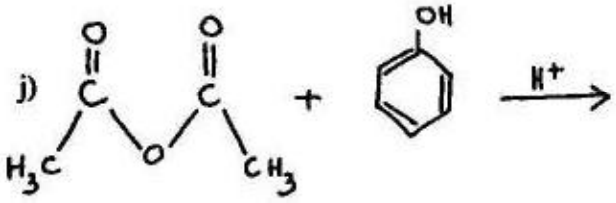
Marks or Minutes	Questions:

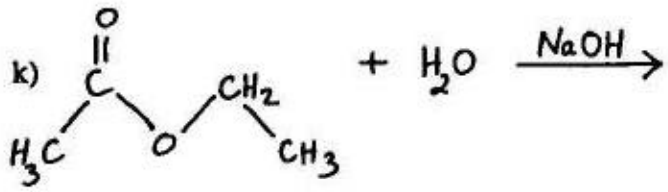
2 f) 

2 g) 

2 h) 

2 i) 

2 j) 

2 k) 

Marks or Minutes	Questions:

3 **2.** Rank the following compounds in order of increasing boiling points
a) diethylamine
b) propanoic acid
c) pentane
d) 1-butanol
e) ethylamine

2 **3.** Rank the following carbocations in order of decreasing stabililty

a) $CH_3\overset{+}{C}H_2$

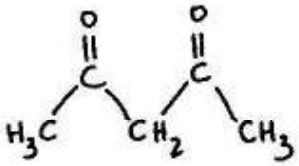
b) $CH_3\overset{+}{C}HCH_3$

c) $CH_3\overset{+}{C}CH_3$ 

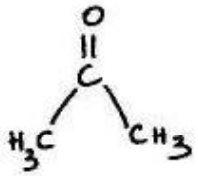
d) $(CH_3)_3\overset{+}{C}$

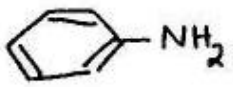
6 **4.** Which compound in each of the following pairs would you expect to be more acidic? Explain your answers.

$Cl_2CHCOOH$ or CH_3COOH

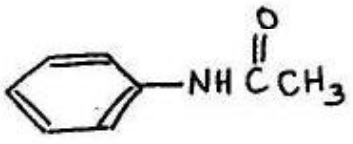


or





or



Marks or Minutes	Questions:

3 **5.** Rank the following compounds in order of decreasing solubility in water

A) $CH_3CH_2CH_2OH$
B) CH_3CH_2COOH
C) $CH_3CH_2CH_2CH_3$
D) $CH_3CH_2CH_3$
E) $CH_3CH_2CH_2NH_2$
F) CH_3CH_2OH

6 **6.** a) How is an hemiacetal formed. Show the reaction mechanism, starting from an aldehyde.

4 b) Show the mechanism by which an hemiacetal is converted to an acetal

2 b) Why are acetals good protecting groups?

Marks or Minutes | Questions:

2 **7.** What alkene will give $CH_3CO(CH_2)_4COOH$ on cleavage with acidic $KMnO_4$?

8. Ascorbic Acid (Vitamin C) does not in fact contain a free carboxylic acid group. It is best described as the internal ester (involving the 4-hydroxy group) of 2,3,4,5,6-pentahydroxy -2-hexenoic acid.

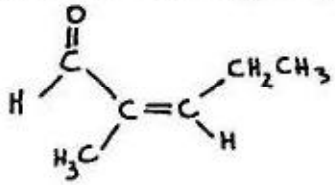
2 a) Draw the structure of 2,3,4,5,6-pentahydroxy-2-hexenoic acid

3 b) Based on the above, next draw the structure of Vitamin C

1 c) Why do internal esters form more readily than do regular esters?

Marks or Minutes	Questions:
4	9. Write the mechanism for a general S_N2 reaction between a nucleophile (Nu^-) and an alkyl halide (include transition state(s), stereochemistry, and intermediates):

10. Consider the following compound: (it is an "enone")



2 Give the IUPAC name of this compound:

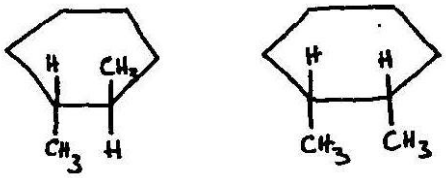
2 Why is this compound relatively stable?

6 What aldehyde could be used to synthesize this molecule via an aldol condensation reaction? Show mechanism

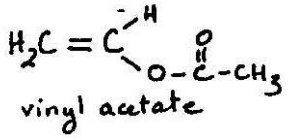
Marks or Minutes | Questions:

2 **11.** What is the relationship between the structures shown below:

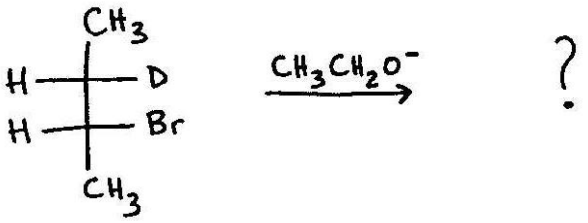
a) conformers
b) enantiomers
c) diasteriomers
d) structural isomers

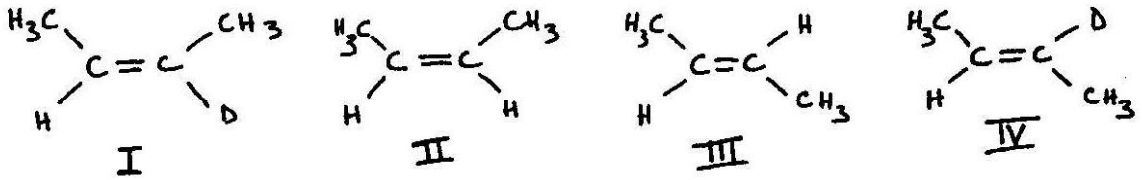


4 **12.** Vinyl acetate undergoes free radical polymerization. Briefly outline a method for the synthesis of polyvinyl alcohol from vinyl acetate:



4 **13.** Circle the correct product(s) of the reaction below: (note D=deuterium)

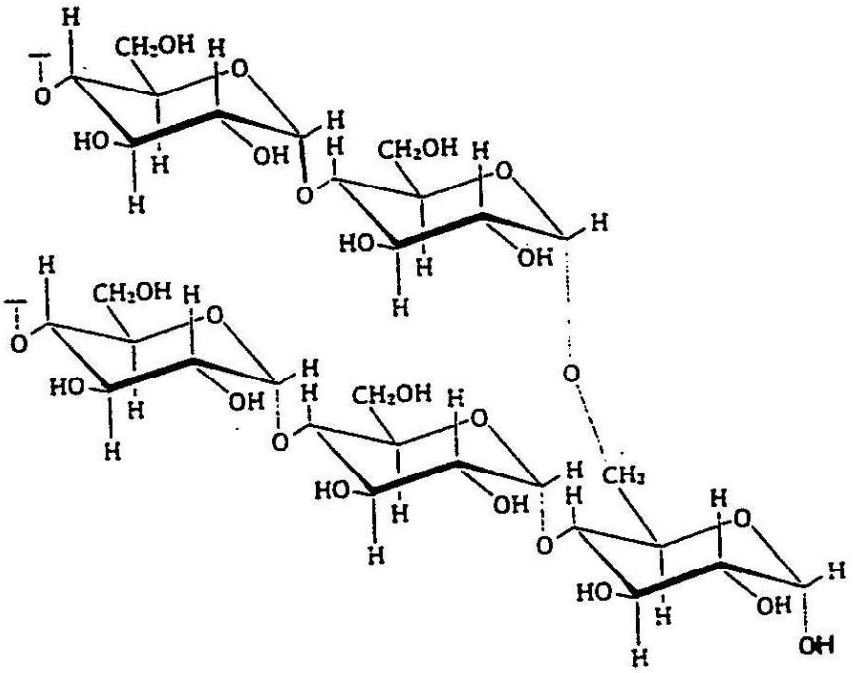




4 **14.** Draw the Fisher projection of any D-aldohexose. Circle the carbon atom that makes this a D-sugar

Marks or Minutes | Questions:

15. The structure of a section of a polymer of glucose is shown below:



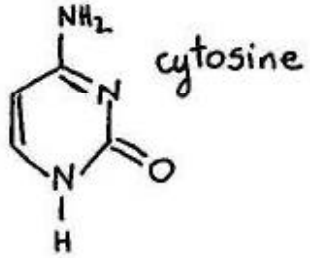
4 a) Use arrows to point to the glycosidic linkage(s) and anomeric carbon(s)in the structure above. What type of linkages do you find (indicate carbon numbers and stereochemistry of each linkage)

3 b) What common polysaccharide(s) could this structure represent? Why?

4 16. When crystals of ß-D-glucopyranose are dissolved in water, the specific rotation changes over a period of time from +112° to +54°. Explain this phenomenon.

Marks or Minutes | Questions:

6 **17.** Draw the structural formula for the nucleotide cytidine 5'-monophosphate. The base component is cytosine (shown below).



18. The sense strand of a particular DNA sequence is given below:

5'-GAGATGTTTGAGTAGCACAC-3'

2 a) How many total hydrogen bonds would exist between the two complementary strands of this piece of DNA?

2 b) What is the sequence of the mRNA transcript?

2 c) What is the sequence of the primary protein product?

2 d) What would happen if a mutation resulted in the deletion of a nucleotide in the DNA sequence?

Marks or Minutes	Questions:

10 **19.** Which of the following statements are true and which are false? Correct false statements.

a) Each codon is composed of four bases

b) DNA polymerase is involved in transcription

c) DNA polymerase catalyzes chain extension in the 5' to 3' direction

d) Each living species is thought to have its own unique genetic code

e) A ß-pleat is an example of a tertiary structure of a protein

f) mRNA is a very stable molecule

g) The Maxam-Gilbert method of DNA sequencing is used in automated sequencing machines

h) Alkaloids are synthetic detergents

i) Restriction endonucleases catalyze vaso-constriction

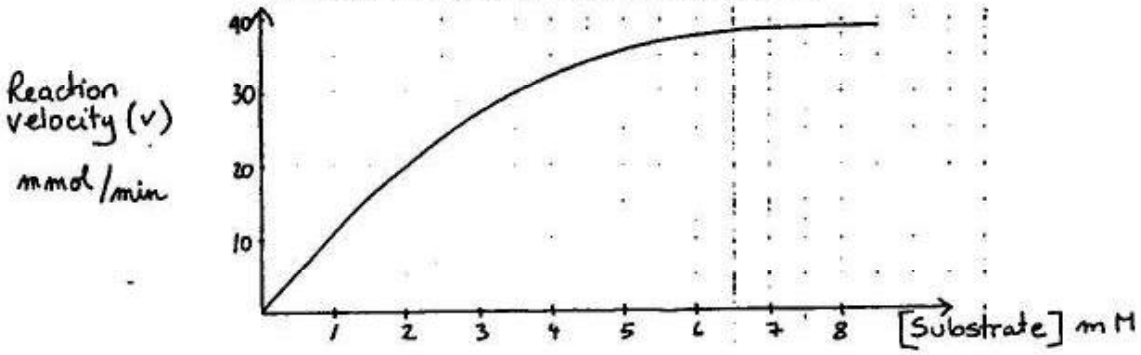
j) Phospholipids are like fats except that one ester group is replaced by a phosphotidylamine

7 **20.** What is the Polymerase Chain Reaction? What reagents are needed in the reaction mixture? Explain the steps involved in one cycle. What fold concentration do you obtain?

Marks or Minutes

Questions:

21. The following is a plot of reaction rate versus substrate concentration for a reaction catalyzed by the enzyme peptidase:



2 a) Why does the rate of an enzyme-catalyzed reaction plateau at a high substrate concentration?

3 b) Estimate K_m and V_{max} for the peptidase enzyme: What property of the enzyme does K_m measure?

2 c) If one doubled the peptidase concentration, what would be the effect on the K_m ?

2 d) What would be the effect of doubling the peptidase concentration on V_{max} ?

Marks or Minutes | Questions:

22. Researchers have found that some bacteria communicate with one another by releasing small peptides into their growth medium. Initially, these peptides were isolated using columns. Most columns are composed of beads which bind to molecules of a particular size or charge, separating them from the original mixture placed on the column. The beads used in the column can be either negatively or positively charged.

Consider the sequence of the peptide (Peptide 1) shown below (N=Amino terminus; C=carboxy terminus):

N-Leu-Arg-Glu-Asn-C

7 a) Draw the structure of Peptide 1 (including the side chains of each amino acid) as it would be found at pH 7.0. Refer to the amino acid structures provided at the end of this exam.

4 b) At pH 7.0, would Peptide 1 carry an overall positive charge, a negative charge or be neutral (uncharged)?

4 c) If the beads used in the column are positively-charged, then at what pH range (between pH 0 - 14) would the majority (>50%) of Peptide 1 bind to these beads? Briefly explain your reasoning. (HINT: Within what pH range would the peptide have a net negative charge?)

Table 16.3 Codon Assignments of Base Triplets

First base (5' end)	*Second base*	*Third base (3' end)*			
		U	*C*	*A*	*G*
U	U	Phe	Phe	Leu	Leu
	C	Ser	Ser	Ser	Ser
	A	Tyr	Tyr	Stop	Stop
	G	Cys	Cys	Stop	Trp
C	U	Leu	Leu	Leu	Leu
	C	Pro	Pro	Pro	Pro
	A	His	His	Gln	Gln
	G	Arg	Arg	Arg	Arg
A	U	Ile	Ile	Ile	Met
	C	Thr	Thr	Thr	Thr
	A	Asn	Asn	Lys	Lys
	G	Ser	Ser	Arg	Arg
G	U	Val	Val	Val	Val
	C	Ala	Ala	Ala	Ala
	A	Asp	Asp	Glu	Glu
	G	Gly	Gly	Gly	Gly

THE END! Have a Great Summer! -Page 14

Table 15.1 Structures of the 20 Common Amino Acids Found in Proteins (Names of the amino acids essential to the human diet are shown in red.)

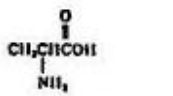
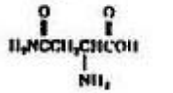
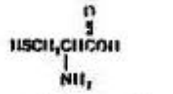
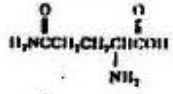
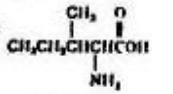
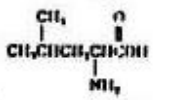
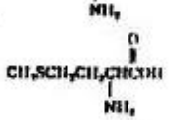
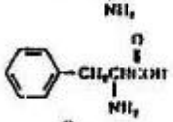
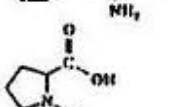
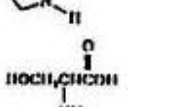
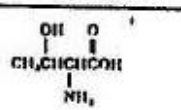
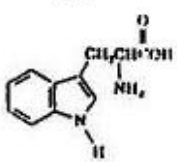
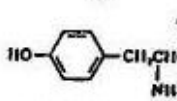
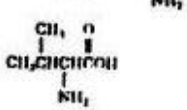
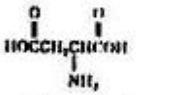
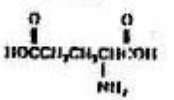
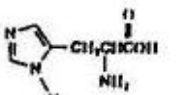
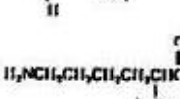
Name	Abbreviations	Molecular weight	Structure	Isoelectric point	pK_{a1} α-COOH	pK_{a2} α-NH_3^+
Neutral Amino Acids						
Alanine	Ala (A)	89		6.00	2.34	9.69
Asparagine	Asn (N)	132		5.41	2.02	8.80
Cysteine	Cys (C)	121		5.07	1.96	10.28
Glutamine	Gln (Q)	146		5.65	2.17	9.13
Glycine	Gly (G)	75		5.97	2.34	9.60
Isoleucine	Ile (I)	131		6.02	2.36	9.60
Leucine	Leu (L)	131		5.98	2.36	9.60
Methionine	Met (M)	149		5.74	2.28	9.21
Phenylalanine	Phe (F)	165		5.48	1.83	9.13
Proline	Pro (P)	115		6.30	1.99	10.60
Serine	Ser (S)	105		5.68	2.21	9.15

Table 15.1 (continued)

Name	Abbreviations	Molecular weight	Structure	Isoelectric point	pK_{a1} α-COOH	pK_{a2} α-NH_3^+
Threonine	Thr (T)	119		5.60	2.09	9.10
Tryptophan	Trp (W)	204		5.89	2.83	9.39
Tyrosine	Tyr (Y)	181		5.66	2.20	9.11
Valine	Val (V)	117		5.96	2.32	9.62
Acidic Amino Acids						
Aspartic acid	Asp (D)	133		2.77	1.88	9.60
Glutamic acid	Glu (E)	147		3.22	2.19	9.67
Basic Amino Acids						
Arginine	Arg (R)	174		10.76	2.17	9.04
Histidine	His (H)	155		7.59	1.82	9.17
Lysine	Lys (K)	146		9.74	2.18	8.95

SIDE CHAIN pK_{a3}:

$\left(-C^{=O}_{OH}\right)$

$pK_{a_3} = 4.4$

→ $pK_{a3} = 12$ $(= \overset{+}{N}H_2)$