UNIVERISTY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING
CHE 391F Organic Chemistry and Biochemistry
Final Exam - Wednesday December 19th, 2001
EXAMINER: Prof. E.A. Edwards

**Answer all questions in the spaces provided. (15 pages; 20 questions; 120 marks)**

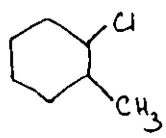
Name______________________________ Student Number:______________________

<u>Marks or Minutes</u> <u>Questions:</u>

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

2 a) $HC \equiv C-CH_2-CH_3 + H_2 \xrightarrow[\text{cat.}]{\text{Lindlar}}$

2 b) $HC \equiv C-CH_2-CH_3 + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

2 c)  $+ KOH \longrightarrow$

2 d)  $-CH_2Cl + CH_3O^- Na^+ \longrightarrow$

| Marks or Minutes | Questions: |
|---|---|
| 2 | e) $CH_3CH_2CH_2Br \; + \; CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}}-O^-K^+ \longrightarrow$ |
| 2 | f) n-butane + $O_2 \longrightarrow$ |
| 2 | g) $CH_3CH_2-\underset{I}{\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}}-CH_3 \; + \; CH_3CH_2OH \longrightarrow$ |
| 3 | h) $CH_2{=}CH-CH{=}CH_2 \; + \; HBr \longrightarrow$ |
| 3 | i) $2\; CH_3-C(=O)-OCH_2CH_3 \xrightarrow[2.\ H_3O^+]{1.\ Na^+\,{}^-OCH_2CH_3}$ |

| Marks or Minutes | Questions: |
|---|---|
| 3 | **2.** Rank the following compounds in order of increasing boiling points<br>a) diethylamine<br>b) propanoic acid<br>c) pentane<br>d) 1-butanol<br>e) ethylamine |
| 6 | **3.** Which compound in each of the following pairs would you expect to be more acidic? Explain your answers. |

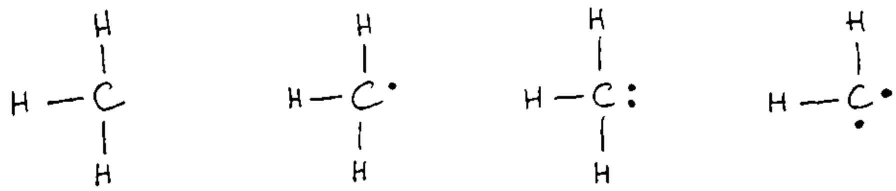
benzoic acid vs p-bromobenzoic acid

cyclohexanol vs phenol

$R-NH_2$ vs $R-C(=O)-NH_2$

| Marks or Minutes | Questions: |
|---|---|
| 3 | **4.** Rank the following compounds in order of decreasing solubility in water<br>a. $CH_3CH_3CH_2OH$<br>b. $CH_3CH_2COOH$<br>c. $CH_3CH_3CH_2CH_3$<br>d. $CH_3CH_3CH_3$<br>e. $CH_3CH_2CH_2NH_2$<br>f. $CH_3CH_2OH$ |
| 4 | **5.** a. How is an hemiacetal formed? Show the reaction mechanism, starting from an aldehyde. |
| 2 | b. Show the mechanism by which an hemiacetal is converted to an acetal |
| 2 | c. Why are acetals good protecting groups? |

| Marks or Minutes | Questions: |
|---|---|
| 4 | 6. Consider each of the following highly reactive carbon species. What is the formal charge on the carbon in each species? |

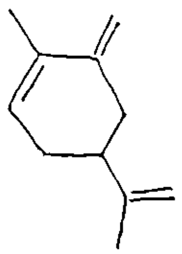


| | |
|---|---|
| 6 | 7. Draw the important resonance contributors for the intermediate in the bromination of aniline, and explain why ortho-para substitution predominates. |

| Marks or Minutes | Questions: |
| --- | --- |
| 6 | **8.** Show a mechanism to synthesize 2-bromo-4-nitrotoluene from toluene. |

**9.** The odors of caraway seeds and mint leaves arise from the enantiomers of carvone (caraway seeds = left; mint leaves = right).

6 a) Identify the stereogenic centre and draw the two enantiomers of carvone in any appropriate projection and identify them as R or S.



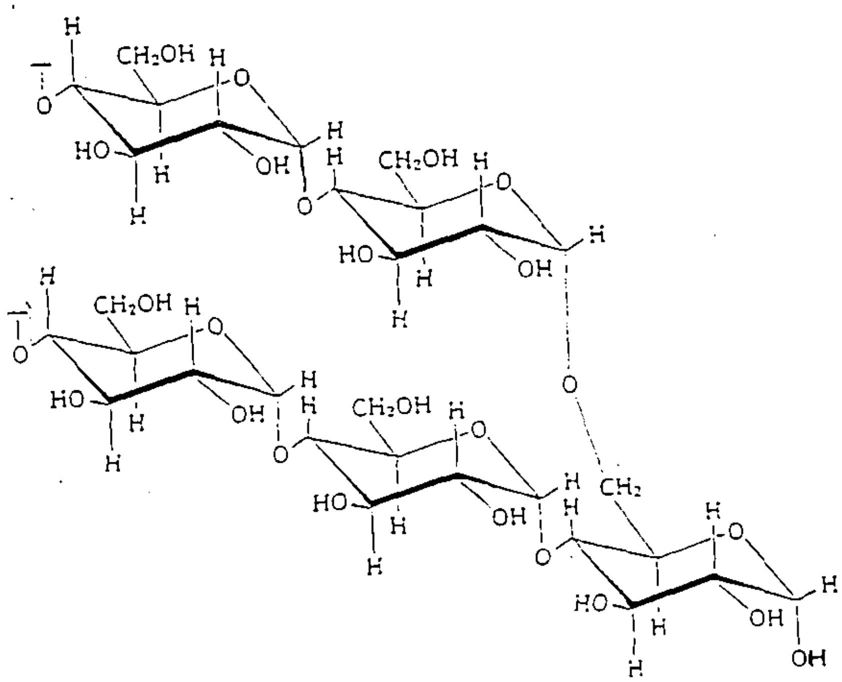
Carvone

2 b) In which direction will each of these enantiomers rotate light?

2 c) Suggest a possible explanation for why these two enantiomers have very different odors.

| Marks or Minutes | | Questions: |
|---|---|---|
| 4 | 10. | Caryophyllene is an unsaturated hydrocarbon mainly responsible for the odor of the oil of cloves. It has the molecular formula $C_{15}H_{24}$. Hydrogenation of caryophyllene gives a saturated hydrocarbon, $C_{15}H_{28}$. Does caryophyllene contain any rings? How many? What else can be learned about the structure of caryophyllene from its hydrogenation? |
| 6 | 11. | Show a complete mechanism for acid-catalyzed keto-enol tautomerization. |

| Marks or Minutes | Questions: |
|---|---|
| 3 | **12.** Draw the Fisher projection of any D-aldohexose. Circle the carbon atom that makes this a D-sugar |
| 4 | **13.** The structure of a section of a polymer of glucose is shown below. Use arrows to point to the glycosidic linkage(s) and anomeric carbons in the structure. Identify the type of linkages between glucose units (indicate carbon numbers and stereochemistry of each). What could this polymer be? |

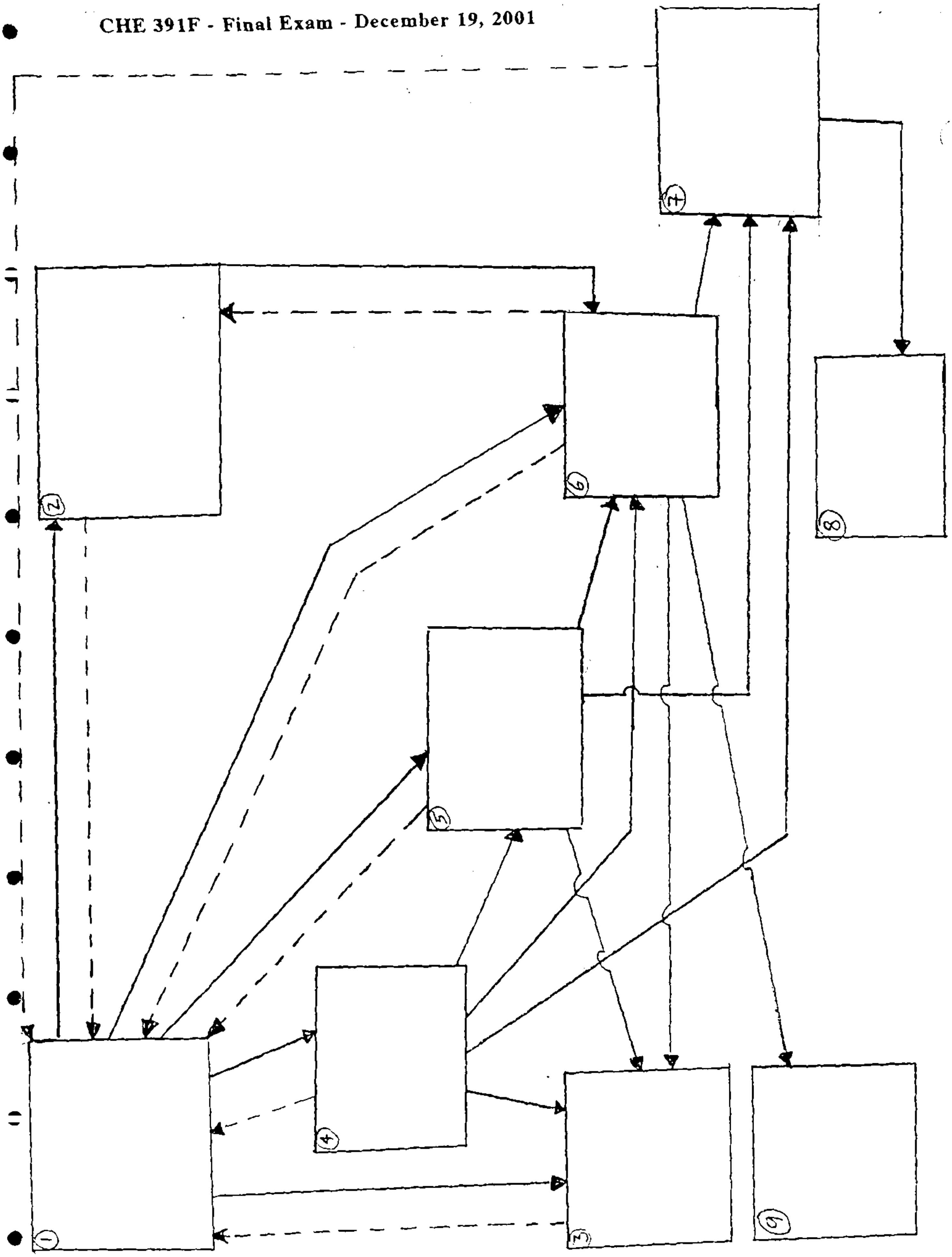


| | |
|---|---|
| 4 | **14.** When crystals of ß-D-glucopyranose are dissolved in water, the specific rotation changes over a period of time from +112° to +54°. Explain this phenomenon. |

| Marks or Minutes | | Questions: |
|---|---|---|
| 13 | **15.** | Complete the table on the next page, summarizing the reactions of carboxylic acids and derivatives. Write all reactions and reagents as we did in class. |

**The following clues apply:**

- Structure 6 is formed from structure 1 by Fisher Esterification
- Structures 3 and 8 are reduced products
- Structure 9 is an alcohol with two identical substituents
- You can wash your face with structure 2.


1
2
3
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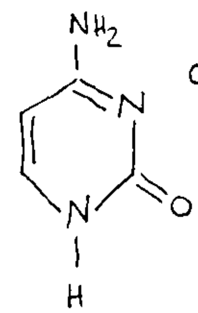
| Marks or Minutes | | Questions: |
|---|---|---|
| 6 | 16. | Draw the structural formula for the nucleotide cytidine 5'-monophosphate. The base component is cytosine (shown below). |




cytosine

17. One strand of a particular DNA sequence is given below:

5'-GAGATGTTTGAGTAGCACAC-3'

2 How many total hydrogen bonds would exist between the two complementary strands of this piece of DNA?
(show your calculation)

| Marks or Minutes | Questions: |
|---|---|
| 3 | **18.** How are phenols synthesized? Briefly outline the 2 steps needed.<br>→ from aromatic compounds |
| 5 | **19.** Which of the following statements are true and which are false?<br>**Correct false statements.** |

a) Many diseases are caused by defective enzymes

b) RNA polymerase is involved in replication

c) Nylon is an addition polymer

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

e) A $\alpha$-helix is an example of a tertiary structure of a protein

f) Morphine is one of the most effective pain killers known

g) An epoxide is a stable ring structure

h) Phenols are useful antioxidants

i) Restriction endonucleases are enzymes that hydrolyze proteins

j) Safety glasses are optional in the lab

| Marks or Minutes | Questions: |
|---|---|

**20.** 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

6 a. Draw the structure of Peptide 1 (including the side chains of each amino acid) as it would be found at pH 7.0. At pH 7.0, would Peptide 1 carry an overall positive charge, a negative charge or be neutral (uncharged)?
**Refer to the amino acid structures provided at the end of this exam.**

| Marks or Minutes | Questions: |
|---|---|
| 3 | b. 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?) |
| 2 | c. If the beads used in the column are negatively-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. |
| 3 | d. You later isolate a version of the peptide, called Peptide 2, with the following sequence: |

N-Leu-Arg-Glu-Asp-C

In this peptide, the side-chain of Glu in Peptide 2 now has a slightly higher pKa than in Peptide 1 shown earlier. Provide an explanation for these observations. (HINT: Draw the structure of Peptide 2.)

THE END

(Amino acid structures on next page)

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.]

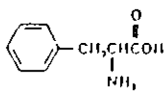
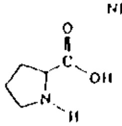
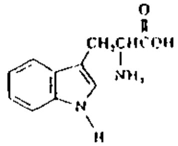
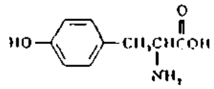
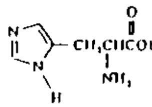
| Name | Abbreviations | Molecular weight | Structure | Isoelectric point | $pK_{a1}$ α-COOH | $pK_{a2}$ α-$NH_3^+$ |
|---|---|---|---|---|---|---|
| **Neutral Amino Acids** | | | | | | |
| Alanine | Ala (A) | 89 | $CH_3CH(NH_2)COOH$ | 6.00 | 2.34 | 9.69 |
| Asparagine | Asn (N) | 132 | $H_2NC(=O)CH_2CH(NH_2)COOH$ | 5.41 | 2.02 | 8.80 |
| Cysteine | Cys (C) | 121 | $HSCH_2CH(NH_2)COOH$ | 5.07 | 1.96 | 10.28 |
| Glutamine | Gln (Q) | 146 | $H_2NC(=O)CH_2CH_2CH(NH_2)COOH$ | 5.65 | 2.17 | 9.13 |
| Glycine | Gly (G) | 75 | $CH_2(NH_2)COOH$ | 5.97 | 2.34 | 9.60 |
| Isoleucine | Ile (I) | 131 | $CH_3CH_2CH(CH_3)CH(NH_2)COOH$ | 6.02 | 2.36 | 9.60 |
| Leucine | Leu (L) | 131 | $CH_3CH(CH_3)CH_2CH(NH_2)COOH$ | 5.98 | 2.36 | 9.60 |
| Methionine | Met (M) | 149 | $CH_3SCH_2CH_2CH(NH_2)COOH$ | 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 | $HOCH_2CH(NH_2)COOH$ | 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 | $CH_3CH(OH)CH(NH_2)COOH$ | 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 | $CH_3CH(CH_3)CH(NH_2)COOH$ | 5.96 | 2.32 | 9.62 |
| **Acidic Amino Acids** | | | | | | |
| Aspartic acid | Asp (D) | 133 | $HOC(=O)CH_2CH(NH_2)COOH$ | 2.77 | 1.88 | 9.60 |
| Glutamic acid | Glu (E) | 147 | $HOC(=O)CH_2CH_2CH(NH_2)COOH$ | 3.22 | 2.19 | 9.67 |
| **Basic Amino Acids** | | | | | | |
| Arginine | Arg (R) | 174 | $H_2NC(=NH)NHCH_2CH_2CH_2CH(NH_2)COOH$ | 10.76 | 2.17 | 9.04 |
| Histidine | His (H) | 155 |  | 7.59 | 1.82 | 9.17 |
| Lysine | Lys (K) | 146 | $H_2NCH_2CH_2CH_2CH_2CH(NH_2)COOH$ | 9.74 | 2.18 | 8.95 |

SIDE CHAIN $pK_{a3}$:

Asp, Glu: $(-C(=O)OH)$ $pK_{a3} = 4.4$

Arg: $\rightarrow pK_{a3} = 12$ $(=\overset{+}{N}H_2)$