For Examiner use only

Q1	
Q2	
Q3	
Q4	
Q5	
Q6	
Total 130	

UNIVERSITY OF TORONTO
Faculty of Applied Science and Engineering
FINAL EXAMINATION, April 25, 2001
Program 06
CHE207S, APPLIED CHEMISTRY III (Organic Chemistry II)
Examiner: D.G.B. Boocock
Time: 2 ½ Hours

STUDENT NAME: ________________________________

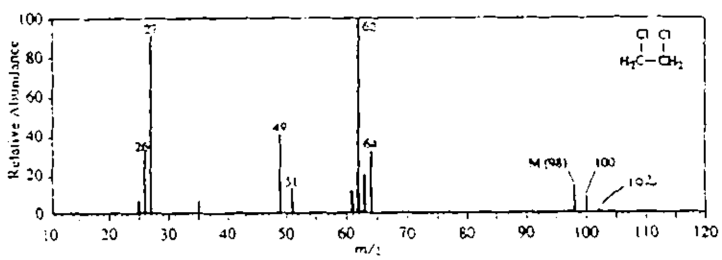
STUDENT NUMBER: ________________

ANSWER ALL QUESTIONS IN THE SPACE PROVIDED: Note that Question 1 is worth 35 marks. Questions 2-6 are worth 20 marks each.

MARKS or MINUTES

(4) **Q1.** (a) Fill in the blanks in the following:
In positive ion mass spectrometry it is difficult to get samples inside the mass spectrometer because of the ________________ ________________ inside the instrument.
The molecules are ionized to molecular ions using a high energy beam of ________________. Some of the molecular ions break up to yield fragment ions. In order to separate the ions (and measure their masses), they are first ________________ across a potential difference, and then ________________ in a magnetic field, according to their momentums.

(6) (b) The positive ion mass spectrum shown below is that of 1,2-dichloroethane, $Cl.CH_2CH_2Cl$. In the boxes provided draw acceptable structures for the ions at m/z 102, 100, 98, 64, 62, 51, 49, 27 and 26 (be careful)



m/z 102 | m/z 100 | m/z 98

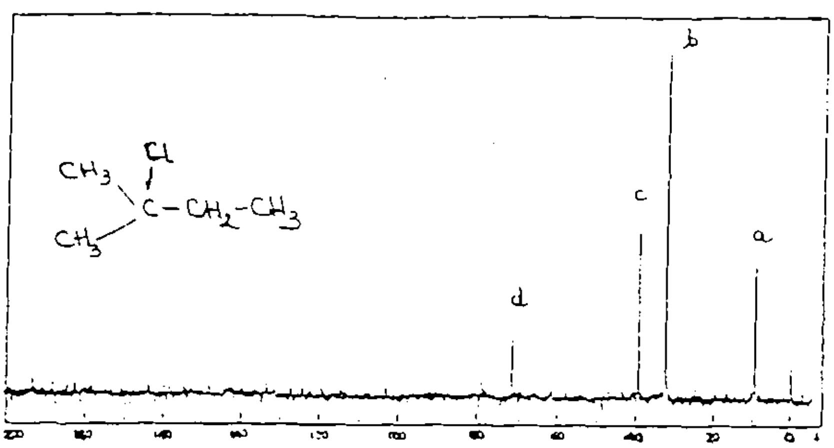
m/z 64 | m/z 62 | m/z 51

m/z 49 | m/z 27 | m/z 26

(3) (c) Describe <u>one</u> of the two methods to obtain the infrared spectrum of an insoluble organic compound.

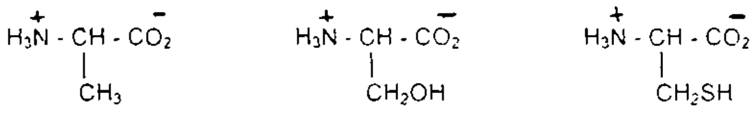
(2) (d) Describe <u>one</u> method to confirm that a signal in a proton nmr spectrum is caused by an OH. Explain what causes the observed effect.

(5) (d) The decoupled ^{13}C-nmr spectrum of 2-chloro-2-methylbutane is as shown. Identify <u>on the structure by letter</u>, the carbon atoms corresponding to each signal. Directly below sketch the partially coupled ^{13}C-nmr spectrum of the same compound (include the TMS signal).



(15) (e) An organic compound X contains 54.54% carbon, 9.09% hydrogen and 37.37% oxygen. The mass spectrum, infrared spectrum and proton nmr spectrum are as shown (see attached sheet). Logically deduce the structure of compound X.

Q2. Proteins and peptides are polymers of twenty naturally occurring α-amino acids. Three of these are shown below. Their isoelectric points are 6.0, 5.7 and 5.0 respectively.



alanine serine cysteine

(2) (a) Draw the major structure of alanine present in aqueous solution at pH 9.

(2) (b) To which electrode(s) will the above three amino acids migrate under electrophoresis at pH 7?

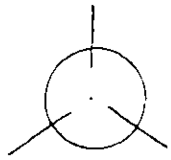
____

Which α-amino acid will travel fastest?

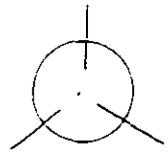
____

(3) (c) Draw the conventional structure of alanylserylcysteine. Circle all the chiral carbon atoms in this tripeptide.

(4) (d) The two circles below represent the chiral carbon atoms in serine and cysteine. For each, put the lowest priority group to the rear. For serine, number the other three groups in order of priority and place them on the carbon atom (according to Cahn-Ingold-Prelog rules) to give the S configuration. For cysteine, number the remaining three groups and place them on the carbon atom to give the R configuration.



serine



cysteine

(3) (e) Only one of the following statements is true when the correct amino acids are filled in the blanks. Choose the true statement and fill in the blanks (think carefully).
When alanylserylcysteine is incubated with carboxypeptidase

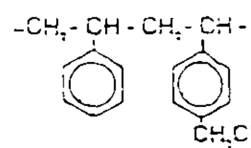
[i] the amino acid ______________ appears first followed by ______________ and then ______________.

[ii] the amino acid ______________ appears first followed by ______________ and ______________ simultaneously (together).

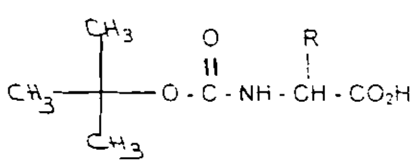
[iii] the amino acids ______________, ______________ and ______________ all appear simultaneously (together).

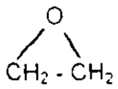
(6) (f) Given the following:

1. Small polystyrene beads containing some p-chlorophenyl groups



2. Sodium hydroxide (aqueous)
3. Dicyclohexylcarbodiimide (DCC) $R_1 - N = C = N - R_1$ $R_1 = C_6H_{11}$)
4. HCl in acetic acid
5. HF in trifluoroacetic acid
6. N-protected alanine, serine and glycine (see general structure below) outline the solid phase Merrifield synthesis of alanyl seryl cysteine. Be clear to state the purpose of DCC (above). To what is it converted when it is used?



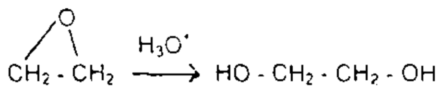
Q3. Ethylene oxide,  is produced in large quantities from ethylene but does not itself have many uses.

(a) Explain why it is made?

(2)

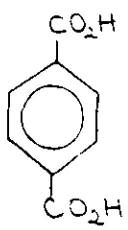
(b) Show the mechanism for the acid-catalyzed ring opening of ethylene oxide to produce 1,2-ethanediol (ethylene glycol)

(3)



(c) Draw the repeating structure in the polyester made from terephthalic acid and ethylene glycol

(2)



$+$ $HO - CH_2 - CH_2 - OH$

(d) Why is it important that the terephthalic acid be pure?

(2)

(e) What general conditions are used to convert para-xylene to terephthalic acid?

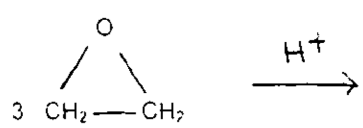
(2)

(f) How is p-xylene separated from the ortho and meta isomers?

(2)

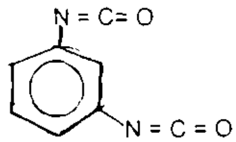
(g) Draw the trimer, formed by the acid catalyzed ring opening of ethylene oxide, that can be used for drying natural gas (note: a little water is required to complete the reaction)

(2)



(h) Draw the <u>repeating</u> structure in the polyurethane made from toluene diisocyanate

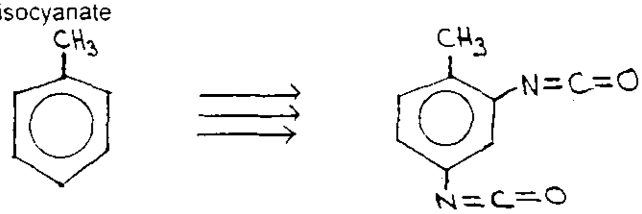
(2)



and ethylene glycol (see previous page)

(i) Show the industrial sequence whereby toluene is converted to toluene diisocyanate

(3)



Q4. (a) [i] Draw the repeating structure present in NYLON 66, the polyamide made from hexamethylene diamine and adipic acid.

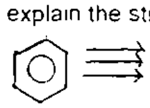
(2)

$H_2N(CH_2)_6NH_2$	$HO_2C(CH_2)_4CO_2H$
hexamethylene diamine	adipic acid

(2) [ii] If solutions of hexamethylene diamine and adipic acid (see above) in methanol are mixed, a solid precipitates. The solid is <u>not</u> Nylon 66. What is the structure of the solid?

(1) What would you do to make Nylon 66 from this solid?

(3) [iii] Outline the steps for the production of adipic acid (see above) starting with benzene. Explain which is the difficult step and explain the strategy used to address the problem.

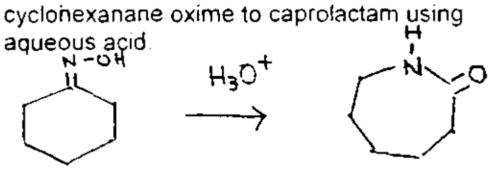


(5) [iv] Outline the steps for the production of hexamethylene diamine from 1,3-butadiene (see above for structure)

$CH_2 = CH - CH = CH_2$

(2) [v] There is insufficient butadiene produced by naphtha cracking to satisfy the demand. What is the other source of butadiene?

(3) (b) [i] Show the mechanism for the rearrangement of cyclohexanane oxime to caprolactam using aqueous acid.



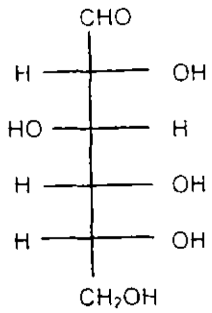
caprolactam

(2) [ii] Draw the repeating structure in Nylon 6, the polyamide resulting from the ring-opening polymerization of caprolactam.

Q5. (a) In the boxes provided, draw the Fischer-projection formulae of the compounds described.

(1.5) [i] Any D-ketopentose

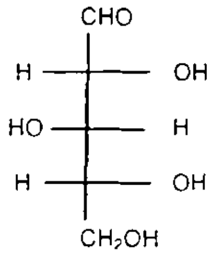
(1.5) [ii] A sugar which forms the same osazone as compound A



A

[iii] A sugar which rotates the plane of polarized light an equal but opposite amount as compound B

(1.5)



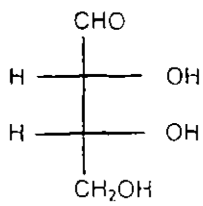
B

[iv] A sugar which forms the same saccharic (aldaric) acid as compound A (see part [ii])

(1.5)

[v] One of the sugars formed by Fischer-Kiliani chain extension of compound D

(1.5)



D

[vi] The C-4 epimer of compound A (see part [ii])

(1.5)

(3) (b) Draw a three-dimensional representation of the chair form of β-D-glucopyranose.
Place all relevant -OH groups in the equatorial positions. Clearly number the carbon atoms according to conventional numbering of sugars.

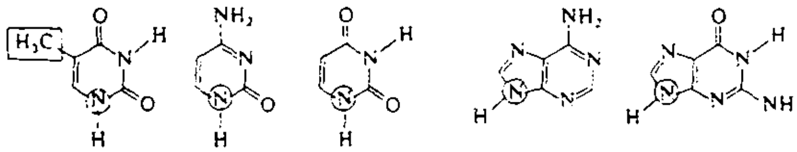
(3) (c) Under the right crystallization conditions, crystals of β-D-glucopyranose can be obtained. When these crystals are dissolved in water, the specific rotation, $[\alpha]_D$, measured immediately is 112°. After a period of time the specific rotation falls to 53° and remains constant. Explain this phenomenon.

(d) When the disaccharide, sucrose, is treated with the enzyme, invertase, the specific rotation changes dramatically from positive to negative. The product is called inverted or partially inverted sugar, of which honey is one example. Explain what is happening.

(e) Starch and cellulose are both polymers of D-glucopyranoses. What is the major difference between the two and what are the implications for digestibility when consumed?

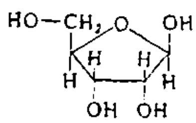
Q6. (a) Given the following structures, explain using diagrams where necessary, the structure of Deoxyribonucleic acids (DNA). What information is contained in DNA and how is that information encoded? (Note: one of the structures below is required for part (b))

(10)

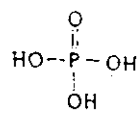


thymine (T) cytosine (C) uracil (U) adenine (A) guanine (G)

pyrimidine bases purine bases



cyclic form of D-ribose



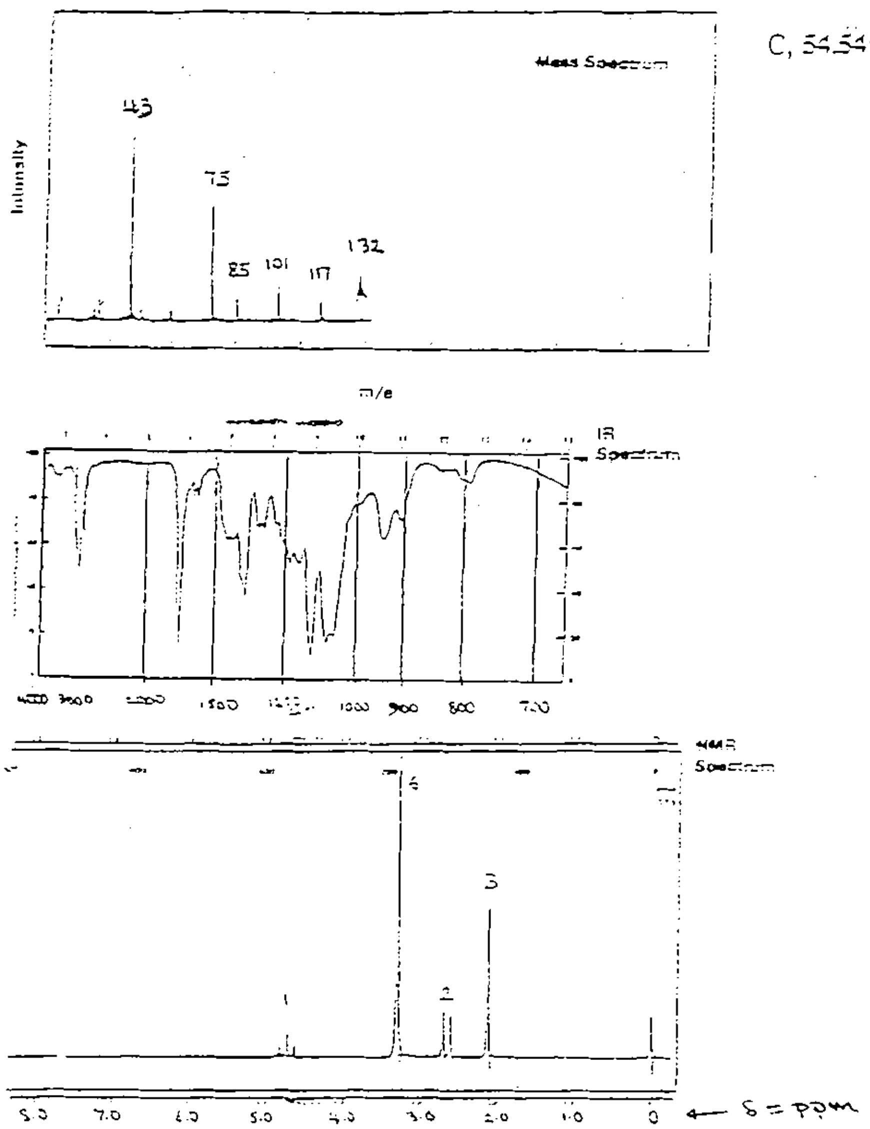
phosphoric acid

(4) (b) Explain how messenger Ribonucleic acids, m-RNA's, are different from DNA. What structural feature of RNA's make them unstable?

(6) (c) Explain how messenger-RNA's and transfer-RNA's are involved in protein synthesis.

ATTACHMENT: Spectra for Compound X (see Question 1(e))

Compound



C, 54.54%; H, 9.09%