Centre Number						Candidate Number				
Surname										
Other Names	Model Answers									
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2010

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 27 January 2010 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. **Answers written in margins or on blank pages will not be marked.**
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

SECTION A

Answer **all** questions in the spaces provided.

1 A mixture was prepared using 1.00 mol of propanoic acid, 2.00 mol of ethanol and 5.00 mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation.

$$CH_3CH_2COOH + CH_3CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_3 + H_2O \qquad \Delta H^{\ominus} = -22\,kJ\,mol^{-1}$$

The equilibrium mixture contained 0.54 mol of the ester ethyl propanoate.

1 (a) (i) Calculate the amounts, in moles, of propanoic acid, of ethanol and of water in this equilibrium mixture.

	CH_3CH_2COOH	+ CH_3CH_2OH	⇌ ester	+ H_2O
I	1.0	2.0	0	5.0
	1.0 − 0.54 = 0.46	2 − 0.54 = 1.46	0.54	5 + 0.54 = 5.54

Moles of propanoic acid 0.46

Moles of ethanol 1.46

Moles of water 5.54

(3 marks)

1 (a) (ii) Write an expression for the equilibrium constant, K_c, for this equilibrium.

$$K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]}$$

(1 mark)

1 (a) (iii) Calculate a value for K_c for this equilibrium at this temperature. Explain why this K_c value has no units.

Calculation $K_c = \frac{0.54 \times 5.54}{0.46 \times 1.46}$ (V cancels out)

$\frac{mol\,dm^{-3} \times mol\,dm^{-3}}{mol\,dm^{-3} \times mol\,dm^{-3}}$

Explanation $K_c = 4.45$ No units! There are no units as equal no. of moles on each side of equation.

(3 marks)

(Extra space)

1 (b) For this equilibrium, predict the effect of an increase in temperature on each of the following.

1 (b) (i) the amount, in moles, of ester at equilibrium

Decrease forward reaction is exothermic (-22) so will move to endothermic side.

(1 mark)

1 (b) (ii) the time taken to reach equilibrium Easier question to get wrong. Rate increases so time decreases!

Decrease

(1 mark)

1 (b) (iii) the value of K_c Equilibrium position shifts left so Kc gets smaller.

Decrease

(1 mark)

10

Turn over for the next question

2 In this question, give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for the term pH.

$-\log[H^+]$

(1 mark)

2 (a) (ii) Calculate the concentration, in mol dm^{-3}, of an aqueous solution of sulfuric acid that has a pH of 0.25

$10^{-0.25} = 0.56$ $[H^+] = 0.56 \text{ mol dm}^{-3}$ diprotic acid

$2H^+$ released so conc is $\frac{H^+}{2}$!!

$\frac{0.56}{2} = 0.28 \text{ mol dm}^{-3}$

(2 marks)

2 (b) A student carried out a titration by adding an aqueous solution of sodium hydroxide from a burette to an aqueous solution of ethanoic acid. The end-point was reached when 22.60 cm^3 of the sodium hydroxide solution had been added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

2 (b) (i) Write an equation for the reaction between sodium hydroxide and ethanoic acid.

$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

(1 mark)

2 (b) (ii) Calculate the concentration, in mol dm^{-3}, of the sodium hydroxide solution used.

$\text{conc.} = \frac{\text{mol}}{\text{vol}}$ conc. x vol = mol $0.410 \times \left(\frac{25}{1000}\right) = 0.01025$ moles of CH_3COOH

1 : 1 ∴ 0.01025 moles of NaOH $\frac{0.01025}{\left(\frac{22.60}{1000}\right)} = 0.454$

(2 marks)

2 (b) (iii) A list of indicators is shown below.

Indicator	pH range
thymol blue	1.2–2.8
bromophenol blue	3.0–4.6
litmus	5.0–8.0
cresol purple	7.6–9.2

Select from the list the most suitable indicator for the end-point of this titration.

Cresol purple the equivalence point of weak acid and strong base is between these points.

(1 mark)

2 (b) (iv) Suggest why the concentration of sodium hydroxide in a solution slowly decreases when left open to air.

NaOH can react with CO_2 in the air. CO_2 is a slightly acidic gas.

(1 mark)

2 (c) At 298 K, the value of the acid dissociation constant, K_a, for ethanoic acid in aqueous solution is 1.74×10^{-5} mol dm^{-3}

2 (c) (i) Write an expression for the acid dissociation constant, K_a, for ethanoic acid.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

(1 mark)

2 (c) (ii) Calculate the pH of 0.410 mol dm^{-3} ethanoic acid at this temperature.

Remember that for a weak acid $[H^+]=[A^-]$

$$1.74\times10^{-5} = \frac{[H^+][CH_3COO^-]}{0.410} \qquad 1.74\times10^{-5}\times0.410 = [H^+]^2$$

$$\sqrt{1.74\times10^{-5}\times0.410} = [H^+] = 2.67\times10^{-3} \qquad -\log[H^+] = 2.57$$

(3 marks)

(Extra space)

Question 2 continues on the next page

2 (c) (iii) Calculate the pH of the buffer solution formed when 10.00 cm^3 of 0.100 mol dm^{-3} potassium hydroxide are added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

Lots going on in this question!

When base acts with weak acid a conjugate salt forms - this is $[A^-]$.

Conc. x vol = moles $0.100 \times \left(\frac{10}{1000}\right) = 1 \times 10^{-3}$ moles KOH

$0.410 \times \left(\frac{25}{1000}\right) = 1.025 \times 10^{-2}$ moles CH_3COOH

Calculate which is in excess.

$KOH + CH_3COOH \rightarrow CH_3COOK + H_2O$

$1.025 \times 10^{-2} - 1 \times 10^{-3} = 9.25 \times 10^{-3}$ moles of CH_3COOH in excess

1×10^{-3} moles of CH_3COOK formed!

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COOK \rightleftharpoons CH_3COO^- + K^+$

Don't forget to convert to concentrations.

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ $\frac{1 \times 10^{-3}}{(35/1000)} = 0.0285$ mol dm^{-3} *(6 marks)*

(Extra space) $\frac{9.25 \times 10^{-3}}{(35/1000)} = 0.264$ mol dm^{-3}

$1.74 \times 10^{-5} = \frac{[H^+] \times 0.0285}{0.264}$ $\frac{1.74 \times 10^{-5} \times 0.264}{0.0285} = [H^+]$

$[H^+] = 1.612 \times 10^{-4}$ $-\log[H^+] = 3.79$

18

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

3 Propanone and iodine react in acidic conditions according to the following equation.

$$CH_3COCH_3 + I_2 \longrightarrow ICH_2COCH_3 + HI$$

A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

3 (a) Give the overall order for this reaction.

Second order

(1 mark)

3 (b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be 1.24×10^{-4} mol dm^{-3} s^{-1}.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3} ← NOT used as not in rate equation.
H^+	0.820

Use these data to calculate a value for the rate constant, k, for the reaction and give its units.

Calculation rate = $k[CH_3COCH_3][H^+]$

$1.24 \times 10^{-4} = k \times 4.40 \times 0.820$

$\frac{1.24 \times 10^{-4}}{4.40 \times 0.820} = k$

$k = 3.44 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}

Units mol dm^{-3} s^{-1} / mol dm^{-3} × mol dm^{-3} = mol^{-1} dm^3 s^{-1}

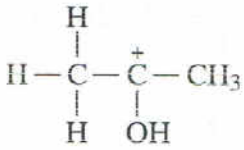
(3 marks)

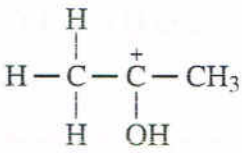
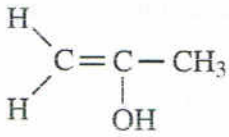
3 (c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.

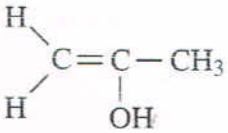
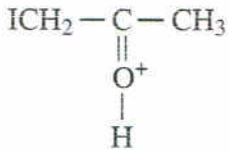
No change - not in rate equation.

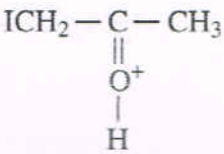
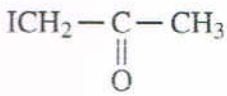
(1 mark)

3 (d) The following mechanism for the overall reaction has been proposed.

Step **1** $CH_3COCH_3 + H^+ \longrightarrow$ 

Step **2**  $\longrightarrow$  $+ H^+$

Step **3**  $+ I_2 \longrightarrow$  $+ I^-$

Step **4**  $\longrightarrow$  $+ H^+$

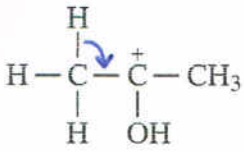
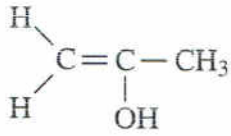
Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

Rate-determining step Step 1

Explanation Both species in rate equation are present.

(2 marks)

3 (e) Use your understanding of reaction mechanisms to predict a mechanism for Step **2** by adding one or more curly arrows as necessary to the structure of the carbocation below.

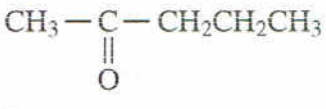
Step **2**  $\longrightarrow$  $+ H^+$

(1 mark)

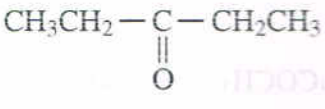
Finishes CH_2 so electron pair must form double bond!

8

4 Two isomeric ketones are shown below.



Q



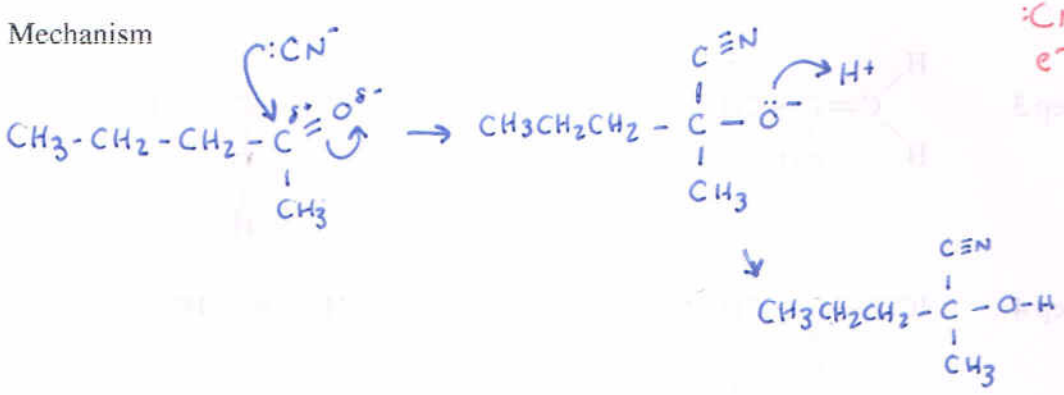
R

4 (a) Name and outline a mechanism for the reaction of compound **Q** with HCN and name the product formed.

Name of mechanism Nucleophilic Addition

Mechanism

:CN⁻ nucleophile e⁻ pair donor.



Name of product 2hydroxy-2methyl-pentanenitrile

don't forget this e.

(6 marks)

4 (b) Some students were asked to suggest methods to distinguish between isomers **Q** and **R**.

One student suggested testing the optical activity of the products formed when **Q** and **R** were reacted separately with HCN.

By considering the optical activity of these products formed from **Q** and **R**, explain why this method would **not** distinguish between **Q** and **R**.

product of R would not form an optically active compound as it does not have a chiral center.

product of Q would form a racemic mixture which is an equal mix of enantiomers and hence will not rotate plane polarised light.

→ equal chance of :CN attacking above or below the plane.

(3 marks)

(Extra space)

product of R: $CH_3CH_2-\underset{\underset{O-H}{|}}{\overset{\overset{C\equiv N}{|}}{C}}-CH_2CH_3$

NOT chiral.

4 (c) Other students suggested using mass spectrometry and the fragmentation patterns of the molecular ions of the two isomers to distinguish between them.

They predicted that only one of the isomers would have a major peak at $m/z = 57$ in its mass spectrum so that this method would distinguish between **Q** and **R**.

4 (c) (i) Identify the isomer that has a major peak at $m/z = 57$ in its mass spectrum.

Isomer R

(1 mark)

4 (c) (ii) Write an equation for the fragmentation of the molecular ion of this isomer to form the species that produces the peak at $m/z = 57$.

$[CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3]^{+\bullet} \rightarrow [CH_3CH_2C{\equiv}O]^{+} + \bullet CH_2CH_3$

(2 marks)

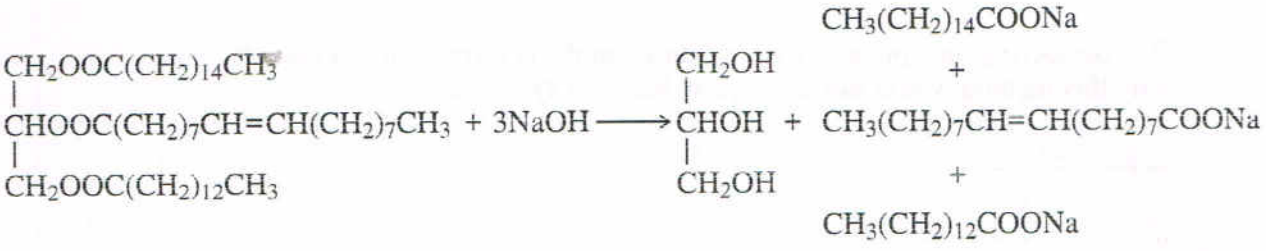
4 (c) (iii) Predict the m/z value of a major peak in the mass spectrum of the other isomer.

71 $[CH_3CH_2CH_2C{\equiv}O]^{+}$

(1 mark)

13

5 The triester, **T**, shown below is found in palm oil. When **T** is heated with an excess of sodium hydroxide solution, the alcohol glycerol is formed together with a mixture of three other products as shown in the following equation.



T glycerol

Also known as saponification - making soap!

5 (a) (i) Give the IUPAC name for glycerol.

propane-1,2,3-triol

(1 mark)

5 (a) (ii) Give a use for the mixture of sodium salts formed in this reaction.

Soap.

(1 mark)

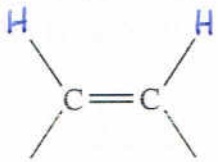
5 (b) When **T** is heated with an excess of methanol, glycerol is formed together with a mixture of methyl esters.

5 (b) (i) Give a use for this mixture of methyl esters.

Biodiesel.

(1 mark)

5 (b) (ii) One of the methyl esters in the mixture has the IUPAC name methyl (*Z*)-octadec-9-enoate. Draw **two** hydrogen atoms on the diagram below to illustrate the meaning of the letter *Z* in the name of this ester.



(1 mark)

5 (b) (iii) One of the other methyl esters in the mixture has the formula $CH_3(CH_2)_{12}COOCH_3$
Write an equation for the complete combustion of one molecule of this ester.

$CH_3(CH_2)_{12}COOCH_3 + 21.5O_2 \rightarrow 15CO_2 + 15H_2O$

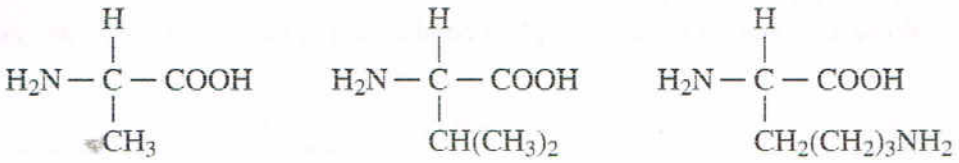
(1 mark)

Be careful! It's not 22.5 as two oxygen atoms in the ester!!

5

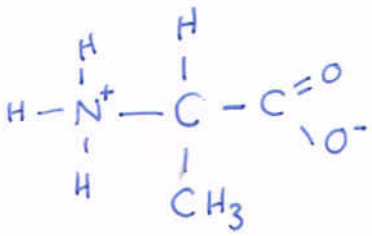
Turn over for the next question

6 The three amino acids shown below were obtained by hydrolysis of a protein.



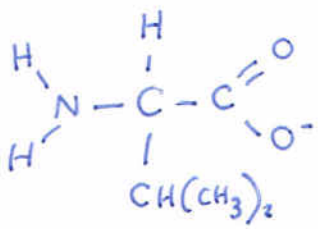
alanine valine lysine

6 (a) (i) Draw the zwitterion of alanine.



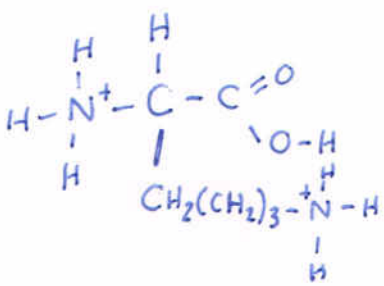
(1 mark)

6 (a) (ii) Draw the species formed when valine is dissolved in an alkaline solution.



(1 mark)

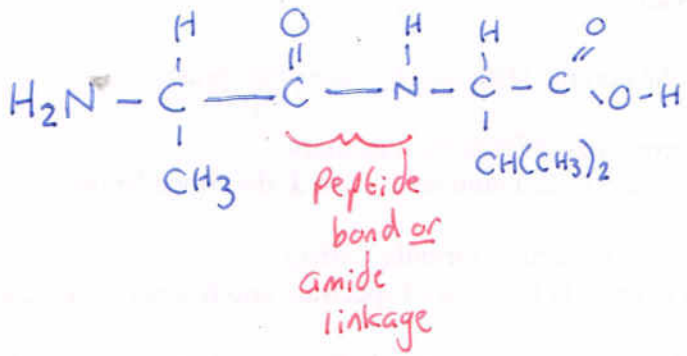
6 (a) (iii) Draw the species formed by lysine at low pH.



Don't forget this $NH_2 \rightarrow NH_3^+$!

(1 mark)

6 (b) Draw the two dipeptides formed by the reaction of alanine with valine.



(2 marks)

6 (c) Name a suitable method by which the mixture of amino acids formed by hydrolysis of the protein can be separated.

chromatography or electrophoresis.

(1 mark)

6

Turn over for the next question

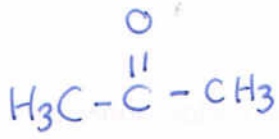
7 Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

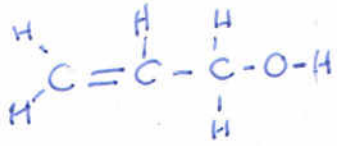
7 (a) Compounds **A** and **B** have the molecular formula C_3H_6O
A has an absorption at 1715 cm^{-1} in its infrared spectrum and has only one peak in its ^1H n.m.r. spectrum.
B has absorptions at 3300 cm^{-1} and at 1645 cm^{-1} in its infrared spectrum and does **not** show *E*–*Z* isomerism.

A



1 peak in ^{1}HNmr as only one Hydrogen environment, H_3C both equivalent.

B

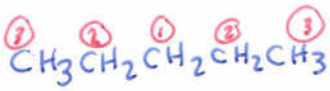


No E-Z isomerism as two hydrogens on same side of double bond.
IR shows 1645 cm^{-1} C=C bond

(2 marks)

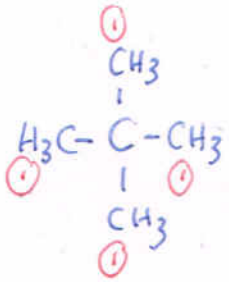
7 (b) Compounds **C** and **D** have the molecular formula C_5H_{12}
In their ^1H n.m.r. spectra, **C** has three peaks and **D** has only one.

C



3 peaks

D

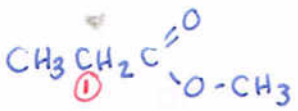


all same environment so one peak

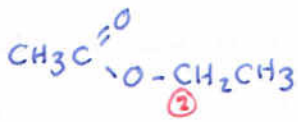
(2 marks)

7 (c) Compounds **E** and **F** are both esters with the molecular formula $C_4H_8O_2$
In their ^1H n.m.r. spectra, **E** has a quartet at $\delta = 2.3$ ppm and **F** has a quartet at $\delta = 4.1$ ppm.

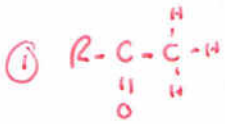
E



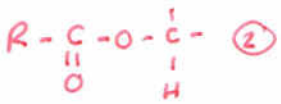
F



2.3 cm^{-1} =



4.1 cm^{-1} =

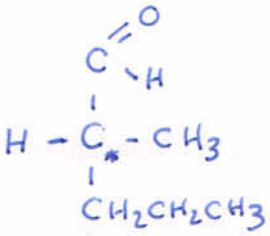


Placement of CH_2 makes spectra different.

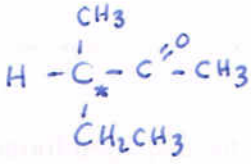
(2 marks)

7 (d) Compounds **G** and **H** have the molecular formula $C_6H_{12}O$
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm^{-1} in its infrared spectrum. **G** forms a silver mirror with Tollens' reagent but **H** does not.

G



H

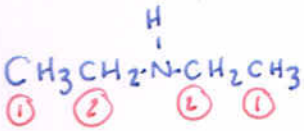


- to be optical both must have a chiral carbon.
- both must have C=O (1700 cm^{-1})
- Tollens forms silver mirror with aldehyde.

(2 marks)

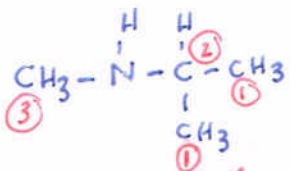
7 (e) Compounds **I** and **J** have the molecular formula $C_4H_{11}N$ and both are secondary amines. In their ^{13}C n.m.r. spectra, **I** has two peaks and **J** has three.

I



two peaks in ^{13}CNMR

J



three peaks in ^{13}CNMR

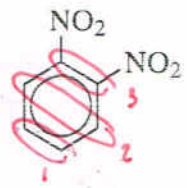
(2 marks)

10

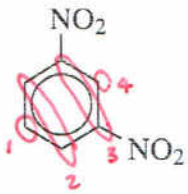
SECTION B

Answer **all** questions in the spaces provided.

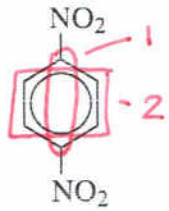
8 Three isomers of $C_6H_4(NO_2)_2$ are shown below.



W



X



Y

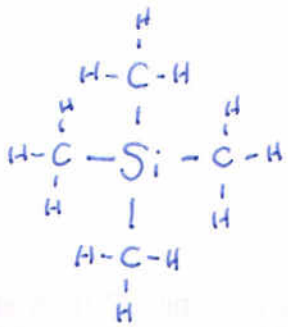
8 (a) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of each isomer.

W = 3 X = 4 Y = 2

(3 marks)

8 (a) (ii) Draw the displayed formula of the compound used as a standard in recording these spectra.

TMS
Tetramethylsilane



(1 mark)

8 (b) Isomer **X** is prepared from nitrobenzene by reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.

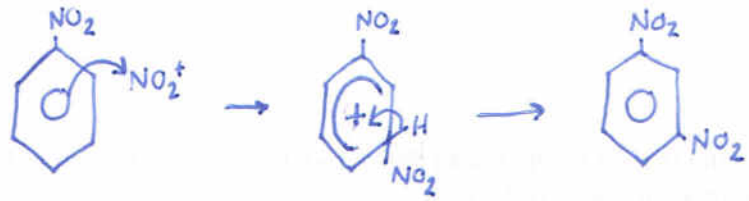
The two acids react to form an inorganic species that reacts with nitrobenzene to form **X**.

8 (b) (i) Give the formula of this inorganic species formed from the two acids and write an equation to show its formation. (1) (2)

NO_2^+ $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

(2 marks)

8 (b) (ii) Name and outline a mechanism for the reaction of this inorganic species with nitrobenzene to form **X**. (1) (2)



Electrophilic Substitution

product should be in para direction for NO_2, as it is electron withdrawing.

(4 marks)

Question 8 continues on the next page

8 (c) Isomer **Y** is used in the production of the polymer Kevlar.

Y is first reduced to the diamine shown below.

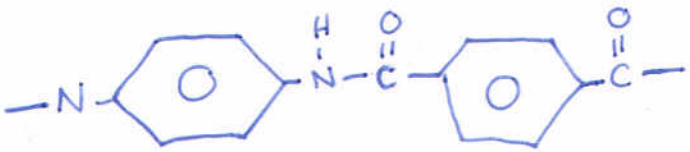
8 (c) (i) Identify a suitable reagent or mixture of reagents for the reduction of **Y** to form this diamine. Write an equation for this reaction using [H] to represent the reducing agent.

Sn/HCl and reflux.

Don't forget the waters to balance this!

(2 marks)

8 (c) (ii) This diamine is then reacted with benzene-1,4-dicarboxylic acid to form Kevlar. Draw the repeating unit of Kevlar.



(2 marks)

8 (c) (iii) Kevlar can be used as the inner lining of bicycle tyres. The rubber used for the outer part of the tyre is made of polymerised alkenes.

State the difference in the biodegradability of Kevlar compared to that of rubber made of polymerised alkenes.

Use your knowledge of the bonding in these polymer molecules to explain this difference.

Kevlar is biodegradeable but the polymerised alkenes are not. Kevlar is polar and contains a peptide bond. This can be attacked by nucleophiles, acids etc, where as the polyalkene is non polar so resistant to attack.

(4 marks)

(Extra space) .....

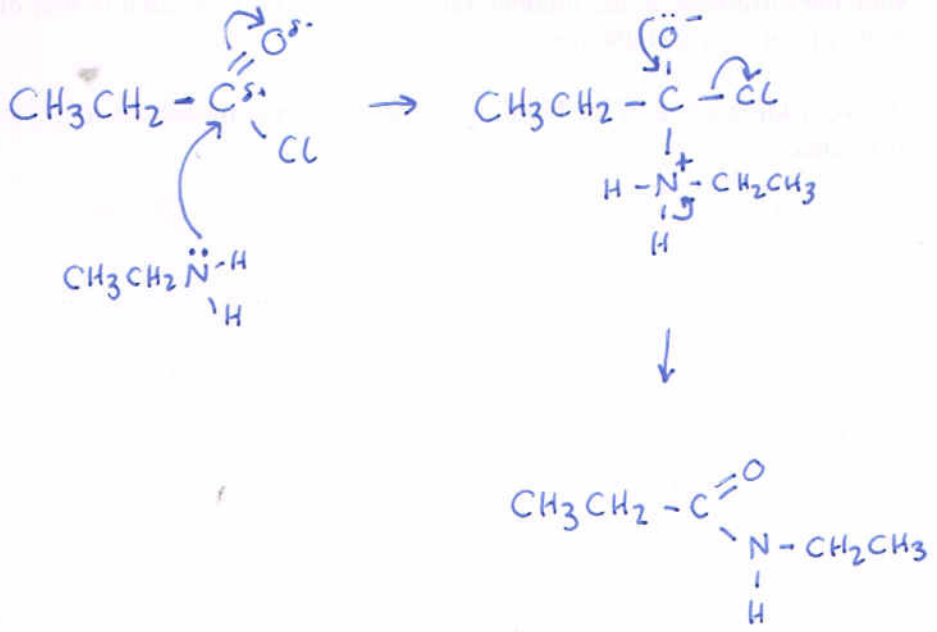
18

Turn over for the next question

9 (a) Name and outline a mechanism for the reaction of $CH_3CH_2NH_2$ with CH_3CH_2COCl

Name the amide formed.

addition-elimination reaction. (1)



N-ethylpropanamide (3)

this is an N substituted amide: where the N atom on the amide has substituted it's H atom.

(6 marks)

amide = $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$

9 (b) Haloalkanes such as CH_3Cl are used in organic synthesis.

Outline a three-step synthesis of $CH_3CH_2NH_2$ starting from methane. Your first step should involve the formation of CH_3Cl

In your answer, identify the product of the second step and give the reagents and conditions for each step.

Equations and mechanisms are **not** required.

firstly free radical substitution of Cl_2 + CH_4.

Cl_2 and UV light to form CH_3Cl.

React this with $KCN_{(aq)}$ in ethanol.

This forms $CH_3C{\equiv}N$.

React this with $LiAlH_4$ and dil. acid to form

Ethylamine $CH_3CH_2NH_2$.

(6 marks)

(Extra space)

Could use H_2/Ni catalyst with High temp + pressure.

12

END OF QUESTIONS