AQA

Please write clearly in block capitals.

Centre number | | | | | | Candidate number | | | | |

Surname NODEL ANSWERS

Forename(s)

Candidate signature

A-level CHEMISTRY

Paper 2 Organic and Physical Chemistry

Monday 19 June 2017 Morning Time allowed: 2 hours

Materials

For this paper you must have:

- the Periodic Table/Data Booklet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator, which you are expected to use where appropriate.

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. Do not write outside the box around each page or on blank pages.
- Do all rough work in this booklet. Cross through any work you do not want to be marked.

Information

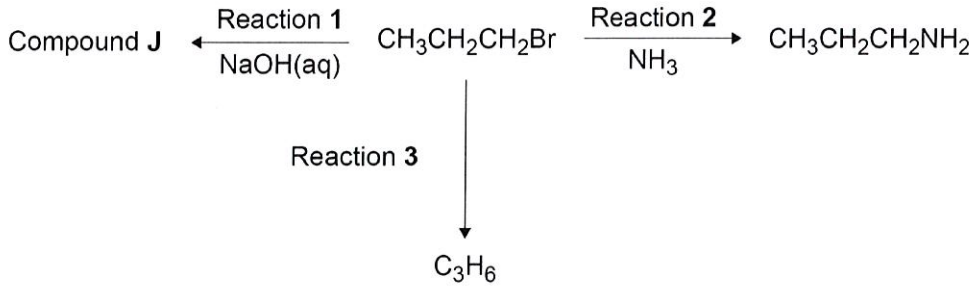
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 105.

For Examiner's Use	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
TOTAL	

Answer **all** questions in the spaces provided

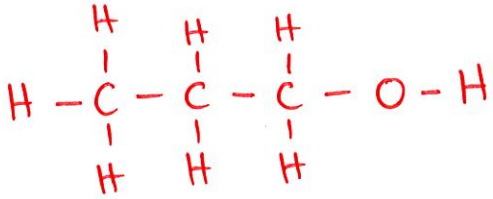
0 1 **Figure 1** shows some compounds made from a halogenoalkane.

Figure 1



0 1 . 1 Draw the displayed formula of compound **J**.

[1 mark]



0 1 . 2 Name the mechanism for Reaction **2** and give an essential condition used to ensure that $CH_3CH_2CH_2NH_2$ is the major product.

[2 marks]

Name of mechanism nucleophilic substitution

Condition excess NH_3

0 1 . 3 Calculate the mass, in grams, of $CH_3CH_2CH_2NH_2$ produced from 25.2 g of $CH_3CH_2CH_2Br$ in Reaction **2** assuming a 75.0% yield.

Give your answer to the appropriate number of significant figures.

[3 marks]

n $CH_3CH_2CH_2Br = \frac{25.2}{122.9} = 0.205$ M1

n $CH_3CH_2CH_2NH_2 = 0.205$

m $CH_3CH_2CH_2NH_2 = 0.205 \times 59 = 12.1\,g$ M2

yield $12.1 \times \frac{75}{100}$

Mass 9.07 g M3

0 1 . 4 When Reaction **2** is carried out under different conditions, a compound with molecular formula $C_9H_{21}N$ is produced.

Draw the skeletal formula of the compound.

Identify the functional group in the compound including its classification.

[2 marks]

Skeletal formula

Functional group including classification 3° amine

0 1 . 5 Identify the reagent and conditions used in Reaction **3**.

[1 mark]

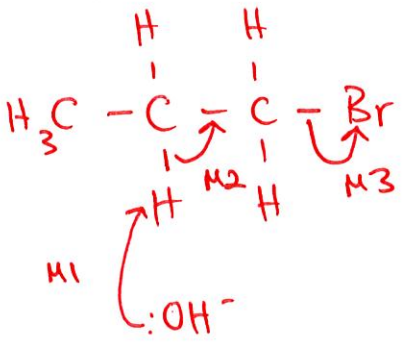
NaOH in ethanol

0 1 . 6 Name and outline a mechanism for Reaction **3**.

[4 marks]

Name of mechanism elimination

Mechanism



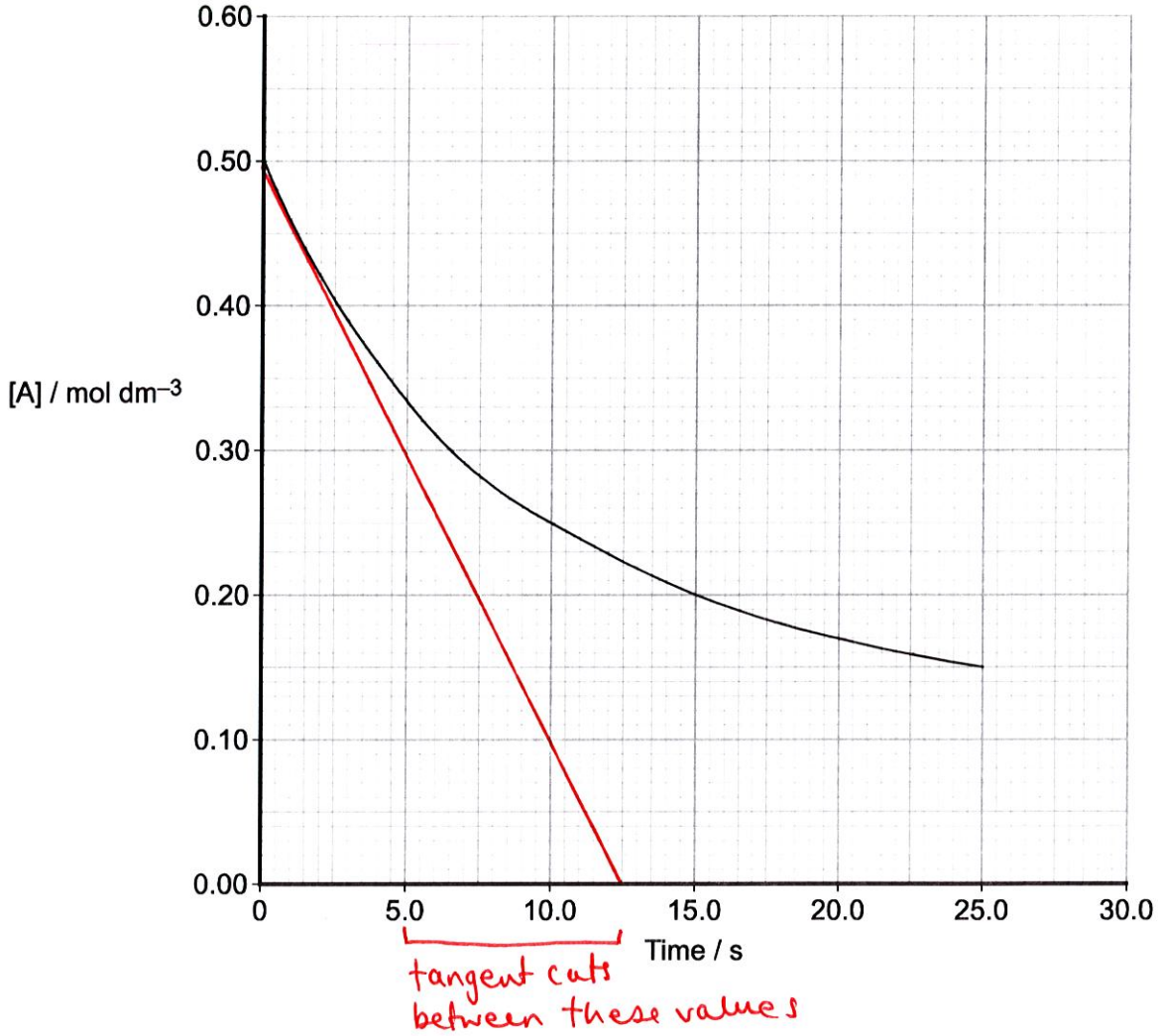
13

0 2 The rate equation for the reaction between compounds **A** and **B** is

$$rate = k[\mathbf{A}]^2[\mathbf{B}]$$

Figure 2 shows how, in an experiment, the concentration of **A** changes with time, t, in this reaction.

Figure 2



0 2 . 1 Draw a tangent to the curve at $t = 0$

[1 mark]

0 2 . 2 Use this tangent to deduce the initial rate of the reaction.

[1 mark]

rate = $\frac{[A]}{t}$ $\frac{0.50}{12.5}$

Initial rate 0.04 mol $dm^{-3}s^{-1}$

0 2 . 3 The experiment was repeated at the same temperature and with the same initial concentration of **B** but with a different initial concentration of **A**.
The new initial rate was 1.7 times greater than in the original experiment.

Calculate the new initial concentration of **A**.

[2 marks]

rate = $k[A]^2[B]$

[A] increased by $\sqrt{1.7} = 1.30$ M1

[A] originally = 0.50

new [A] = 0.50×1.30

Initial concentration of **A** 0.65 mol dm^{-3} M2

4

Turn over for the next question

0 3 A series of experiments is carried out with compounds **C** and **D**. Using the data obtained, the rate equation for the reaction between the two compounds is deduced to be

$$rate = k[\mathbf{C}][\mathbf{D}]$$

In one experiment at 25 °C, the initial rate of reaction is 3.1×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **C** is 0.48 mol dm^{-3} and the initial concentration of **D** is 0.23 mol dm^{-3}

0 3 . 1 Calculate a value for the rate constant at this temperature and give its units.
[3 marks]

$k = \frac{rate}{[C][D]}$ M1

$= \frac{3.1 \times 10^{-3}}{0.48 \times 0.23}$ $\frac{mol\ dm^{-3}\ s^{-1}}{(mol\ dm^{-3})(mol\ dm^{-3})}$

Rate constant 2.8×10^{-2} M2 Units $mol^{-1}\ dm^{-3}\ s^{-1}$ M3

0 3 . 2 An equation that relates the rate constant, k, to the activation energy, E_a, and the temperature, T, is

$$\ln k = \frac{-E_a}{RT} + \ln A$$

Use this equation and your answer from Question **3.1** to calculate a value, in kJ mol^{-1}, for the activation energy of this reaction at 25 °C.

For this reaction $\ln A = 16.9$

The gas constant $R = 8.31$ J K^{-1} mol^{-1}

(If you were unable to complete Question **3.1** you should use the value of 3.2×10^{-3} for the rate constant. This is not the correct value.)

[4 marks]

If $k = 2.8 \times 10^{-2}$

$\ln k = \ln 2.8 \times 10^{-2} = -3.58$ M1

$-Ea = RT(\ln k - \ln A)$ M2

$= 8.31 \times 298 \times (-3.58 - 16.9)$

$= -50716 \times 10^{-3}$ M3

Activation energy 51 kJ mol^{-1} M4

7

0 4 The aldehyde $CH_3CH_2CH_2CH_2CHO$ reacts with KCN followed by dilute acid to form a racemic mixture of the two stereoisomers of $CH_3CH_2CH_2CH_2CH(OH)CN$

0 4 . 1 Give the IUPAC name of $CH_3CH_2CH_2CH_2CH(OH)CN$

[1 mark]

2-hydroxyheexanenitrile

0 4 . 2 Describe how you would distinguish between separate samples of the two stereoisomers of $CH_3CH_2CH_2CH_2CH(OH)CN$

[2 marks]

- plane polarised light M1
- enantiomers rotate light equally in opposite directions M2

0 4 . 3 Explain why the reaction produces a racemic mixture.

[3 marks]

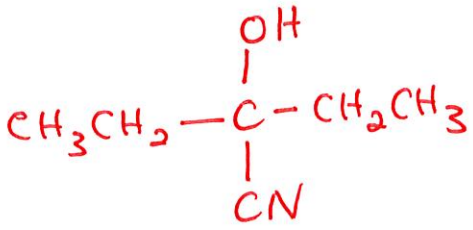
- carbonyl group is planar M1
- nucleophile attacks equally from M2
- both sides M3

0 4 . 4 An isomer of $CH_3CH_2CH_2CH_2CHO$ reacts with KCN followed by dilute acid to form a compound that does not show stereoisomerism.

Draw the structure of the compound formed and justify why it does not show stereoisomerism.

[2 marks]

Structure



Justification

• doesn't have a chiral carbon

or • doesn't have a carbon with 4 different groups

8

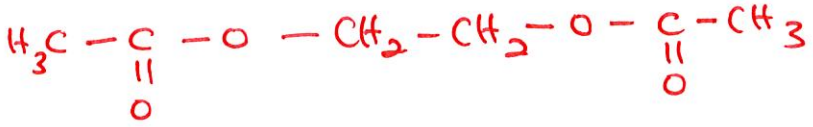
Turn over for the next question

0 5 Ethanoic acid and ethane-1,2-diol react together to form the diester ($C_6H_{10}O_4$) as shown.

$$2CH_3COOH(l) + HOCH_2CH_2OH(l) \rightleftharpoons C_6H_{10}O_4(l) + 2H_2O(l)$$

0 5 . 1 Draw a structural formula for the diester $C_6H_{10}O_4$

[1 mark]



0 5 . 2 A small amount of catalyst was added to a mixture of 0.470 mol of ethanoic acid and 0.205 mol of ethane-1,2-diol.

The mixture was left to reach equilibrium at a constant temperature.

Complete **Table 1**.

Table 1

Amount in the mixture / mol				
	CH_3COOH	$HOCH_2CH_2OH$	$C_6H_{10}O_4$	H_2O
At the start	0.470	0.205	0	0
At equilibrium	0.180	6.00×10^{-2}	0.145	0.29
		M1	M2	M3

[3 marks]

Space for working

$0.470 - 0.180 = 0.29$ change in moles CH_3COOH

ratio $CH_3COOH : H_2O$ 1 : 1

$: HOCH_2CH_2OH$ 2 : 1

$: C_6H_{10}O_4$ 2 : 1

∴ moles eqm $H_2O = 0.29$

$HOCH_2CH_2OH = 0.205 - \left(\frac{0.29}{2}\right)$

$C_6H_{10}O_4 = \frac{0.29}{2}$

0 5 . 3 Write an expression for the equilibrium constant, K_c, for the reaction.

The total volume of the mixture does not need to be measured to allow a correct value for K_c to be calculated.

Justify this statement.

[2 marks]

Expression

$$K_c = \frac{[C_6H_{10}O_4][H_2O]^2}{[CH_3COOH]^2[HOCH_2CH_2OH]}$$ M1

Justification

- Volumes cancel out M2

OR : equal number of moles on each side of equation

0 5 . 4 A different mixture of ethanoic acid, ethane-1,2-diol and water was prepared and left to reach equilibrium at a different temperature from the experiment in Question **5.2**

The amounts present in the new equilibrium mixture are shown in **Table 2**.

Table 2

Amount in the mixture / mol				
	CH_3COOH	$HOCH_2CH_2OH$	$C_6H_{10}O_4$	H_2O
At new equilibrium	To be calculated	0.264	0.802	1.15

The value of K_c was 6.45 at this different temperature.

Use this value and the data in **Table 2** to calculate the amount, in mol, of ethanoic acid present in the new equilibrium mixture.
Give your answer to the appropriate number of significant figures.

[3 marks]

$$[CH_3COOH]^2 = \frac{[C_6H_{10}O_4][H_2O]^2}{K_c[HOCH_2CH_2OH]}$$ M1

$$= \frac{0.802 \times 1.15^2}{6.45 \times 0.264}$$

$$= 0.623$$ M2

$$[CH_3COOH] = \sqrt{0.623}$$

Amount of ethanoic acid 0.789 mol M3

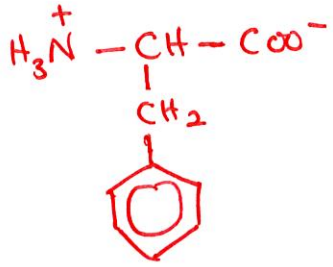
9

0 6 Use the Data Booklet to help you answer this question.

This question is about amino acids and peptide (amide) links.

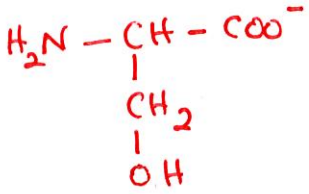
0 6 . 1 Draw the structure of the zwitterion formed by phenylalanine.

[1 mark]



0 6 . 2 Draw the structure of serine at high pH.

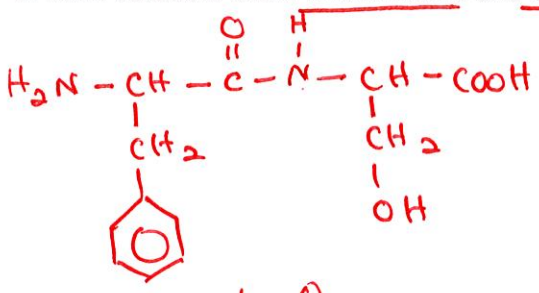
[1 mark]



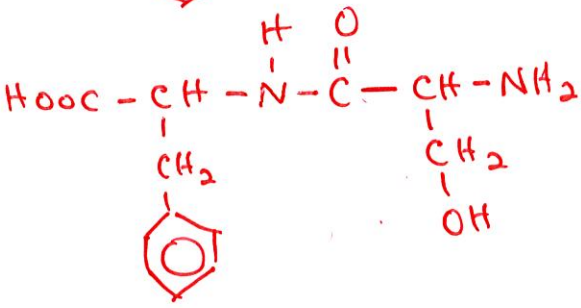
0 6 . 3 Draw the structures of both dipeptides formed when phenylalanine reacts with serine.

In each structure show all the atoms and bonds in the amide link.

[2 marks]



M1



M2

0 6 . 4 An amide link is also formed when an acyl chloride reacts with a primary amine.

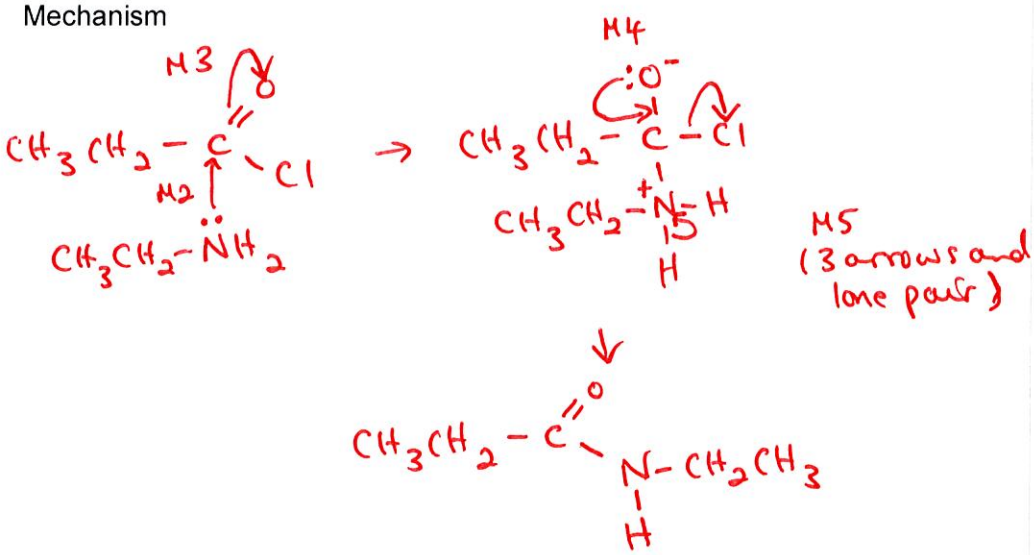
Name and outline a mechanism for the reaction between CH_3CH_2COCl and $CH_3CH_2NH_2$

Give the IUPAC name of the organic product.

[6 marks]

Name of mechanism nucleophilic addition-elimination M1

Mechanism

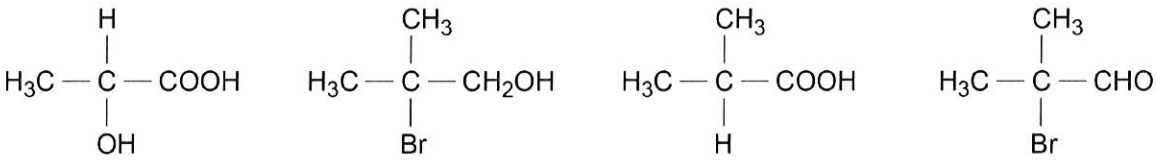


IUPAC name of organic product N-ethylpropanamide M6

10

0 7 Test-tube reactions can be used to identify the functional groups in organic molecules.

0 7 . 1 You are provided with samples of each of the four compounds.



K **L** **M** **N**

Describe how you could distinguish between all four compounds using the minimum number of tests on each compound.

You should describe what would be observed in each test.

LEVELLED

[6 marks]

(Describe test for each functional group)

- COOH
  - $NaHCO_3$. effervence
  - K and M but not L and N
- OH and -CHO
  - acidified $K_2Cr_2O_7$. solution turns green
  - K and N but not M
- CHO
  - Fehlings or Tollens . red ppt or silver mirror
  - N only not K, L, M
- Br
  - $AgNO_3$. cream ppt
  - L and N but not K or M

6

0 8 This question is about nitrobenzenes.

0 8 . 1 Nitrobenzene reacts when heated with a mixture of concentrated nitric acid and concentrated sulfuric acid to form a mixture of three isomeric dinitrobenzenes.

Write an equation for the reaction of concentrated nitric acid with concentrated sulfuric acid to form the species that reacts with nitrobenzene.

[1 mark]

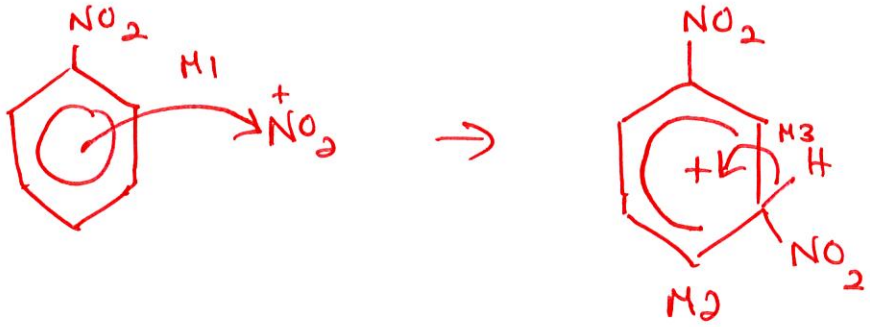
$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

0 8 . 2 Name and outline a mechanism for the reaction of this species with nitrobenzene to form 1,3-dinitrobenzene.

[4 marks]

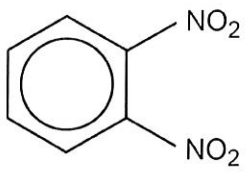
Name of mechanism electrophilic substitution

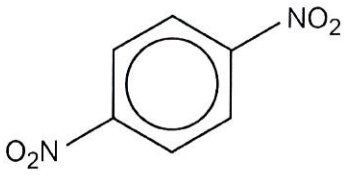
Mechanism



Turn over for the next question

0 8 . 3 The dinitrobenzenes shown were investigated by thin layer chromatography (TLC).

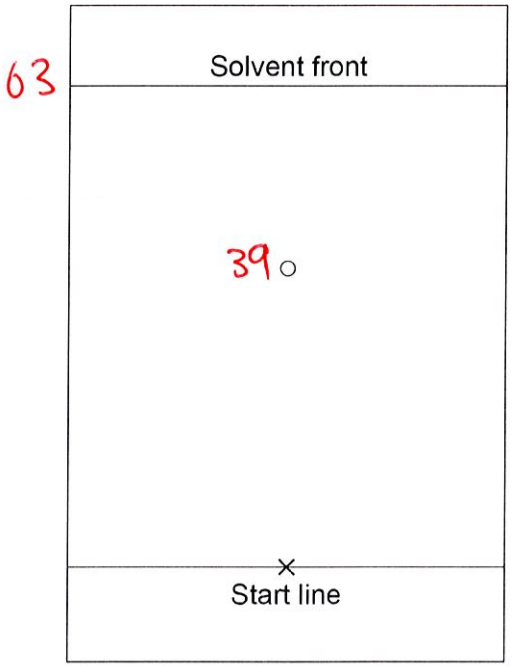




In an experiment, carried out in a fume cupboard, a concentrated solution of pure 1,4-dinitrobenzene was spotted on a TLC plate coated with a solid that contains polar bonds. Hexane was used as the solvent in a beaker with a lid.

The start line, drawn in pencil, the final position of the spot and the final solvent front are shown on the chromatogram in **Figure 3**

Figure 3



Use the chromatogram in **Figure 3** to deduce the R_f value of 1,4-dinitrobenzene in this experiment.

Tick (✓) **one** box.

$\frac{39}{63} = 0.619$

[1 mark]

A 0.41 ☐

B 0.46 ☐

C 0.52 ☐

D 0.62 ☑

0 8 . 4 State in general terms what determines the distance travelled by a spot in TLC.

[1 mark]

affinity for stationary phase and solubility in mobile phase

0 8 . 5 To obtain the chromatogram, the TLC plate was held by the edges and placed in the solvent in the beaker in the fume cupboard. The lid was then replaced on the beaker.

Give one other practical requirement when placing the plate in the beaker.

[1 mark]

solvent must be below the start line

0 8 . 6 A second TLC experiment was carried out using 1,2-dinitrobenzene and 1,4-dinitrobenzene. An identical plate to that in Question **8.3** was used under the same conditions with the same solvent. In this experiment, the R_f value of 1,4-dinitrobenzene was found to be greater than that of 1,2-dinitrobenzene.

Deduce the relative polarities of the 1,2-dinitrobenzene and 1,4-dinitrobenzene and explain why 1,4-dinitrobenzene has the greater R_f value.

[2 marks]

Relative polarities

1,2-dinitrobenzene is more polar

Explanation

1,4-dinitrobenzene was less attracted to the polar plate so it travelled further

0 8 . 7 A third TLC experiment was carried out using 1,2-dinitrobenzene. An identical plate to that in Question **8.3** was used under the same conditions, but the solvent used contained a mixture of hexane and ethyl ethanoate.

A student stated that the R_f value of 1,2-dinitrobenzene in this third experiment would be greater than that of 1,2-dinitrobenzene in the experiment in Question **8.6**

Is the student correct? Justify your answer.

[2 marks]

. Yes

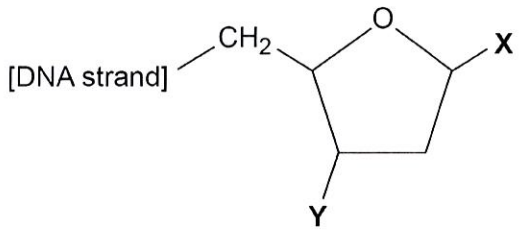
. ethyl ethanoate is polar so in the 3rd experiment 1,2-dinitrobenezene will be more sowble in the mobile phase M2 M1

12

0 9 Use the Data Booklet to help you answer these questions.

DNA exists as two strands of nucleotides in the form of a double helix with hydrogen bonding between the two strands.

0 9 . 1 A deoxyribose molecule in a strand of DNA is shown.



Name the types of group attached to 2-deoxyribose at positions **X** and **Y**.

[2 marks]

X base

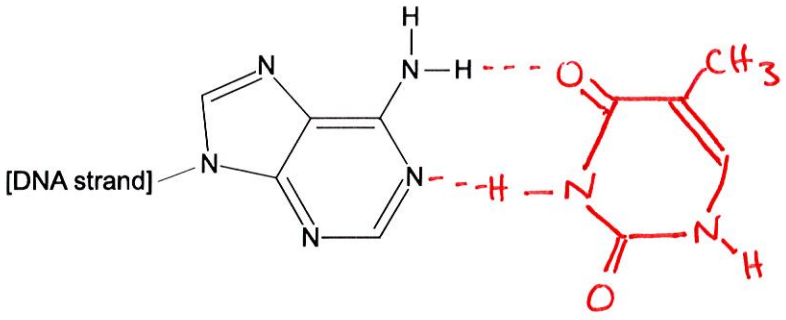
Y phosphate

0 9 . 2 In the DNA double helix, adenine is linked by hydrogen bonds to a molecule in the other strand of DNA.

Complete the diagram below to show the other molecule and the hydrogen bonds between it and adenine.

[2 marks]

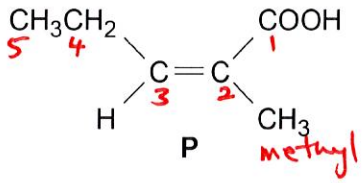
adenine + thymine



4

10 This question is about six isomers of $C_6H_{10}O_2$

10.1 Give the full IUPAC name of isomer **P**.



[1 mark]

2-2-methylpent-2-enoic acid

10.2 A sample of **P** was mixed with an excess of oxygen and the mixture ignited. After cooling to the original temperature, the total volume of gas remaining was 335 cm^3

When this gas mixture was passed through aqueous sodium hydroxide, the carbon dioxide reacted and the volume of gas decreased to 155 cm^3

Both gas volumes were measured at 25 °C and 105 kPa
298 K 105000 Pa

Write an equation for the combustion of **P** in an excess of oxygen and calculate the mass, in mg, of **P** used.

The gas constant $R = 8.31\ J\ K^{-1}\ mol^{-1}$ $M_r\ C_6H_{10}O_2 = 114$

[5 marks]

- $C_6H_{10}O_2 + 7.5O_2 \rightarrow 6CO_2 + 5H_2O$ M1
- vol. $CO_2 = 335 - 155 = 180\ cm^3$ 180×10^{-6} m M2
- $PV = nRT \quad \therefore \quad n = PV/RT$

$$n\ CO_2 = \frac{105000 \times 180 \times 10^{-6}}{8.31 \times 298} = 7.632 \times 10^{-3}$$ M3

- $n\ C_6H_{10}O_2 = 7.632 \times 10^{-3} / 6 = 1.272 \times 10^{-3}$ M4
- $m\ C_6H_{10}O_2 = 1.272 \times 10^{-3} \times 114 = 0.145\ g$

$g \rightarrow mg \times 10^3$

Mass of **P** used 145 mg M5

1 0 . 3 Isomer **Q** ($C_6H_{10}O_2$) is a cyclic compound. The infrared spectrum of **Q** is shown in **Figure 4** and the ^{13}C NMR spectrum of **Q** is shown in **Figure 5.**

Figure 4

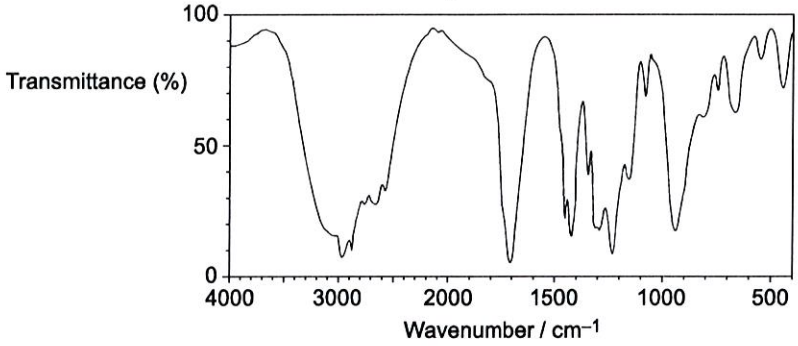
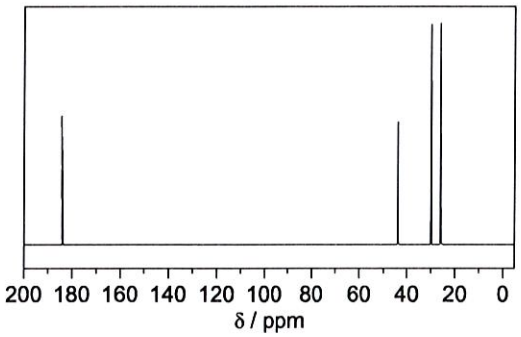


Figure 5



Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.
In your answer, state one piece of evidence you have used from each spectrum.

[3 marks]

Structure of **Q**.

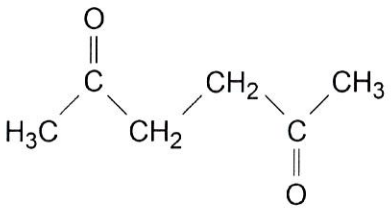
Evidence from **Figure 4**

IR shows peak for OH in an acid (plus peak for C=O)

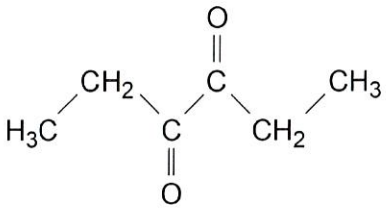
Evidence from **Figure 5**

Peak at ~180 for C=O in acids

1 0 . 4 Isomers **R** and **S** are shown.



R



S

Although the ^{13}C spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using Table **C** from the Data Booklet.

Give the number of peaks for each isomer.

[3 marks]

Justification

- R has 4 C adjacent to C=O giving 2 peaks in range δ = 20-50 M1
- S has 2 C adjacent to C=O giving only 1 peak in range δ = 20-50 M2

Number of peaks Both have 3 peaks M3

Other answers:

- S has $-CH_2-CH_2$ R does not M1
- S has 1 peak in range δ 35-40 R does not M2

1 0 . 5 Although the ^{1}H spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using the splitting patterns of the peaks.

Give the number of peaks for each isomer.

[3 marks]

Justification

- R - singlets only for CH_3 and CH_2 M1
- S - triplet and quartet for CH_3 and CH_2 M2

Number of peaks Both have 2 peaks M3

Question 10 continues on the next page

1 0 . 6 The action of heat on 5-hydroxyhexanoic acid can lead to two different products.

On gentle heating, 5-hydroxyhexanoic acid loses water to form a cyclic compound, **T** ($C_6H_{10}O_2$). form an ester

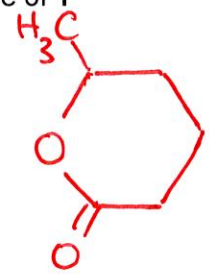
Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

Draw the structure of **T**.

Draw the repeating unit of the polyester and name the type of polymerisation. **[3 marks]**

Not needed

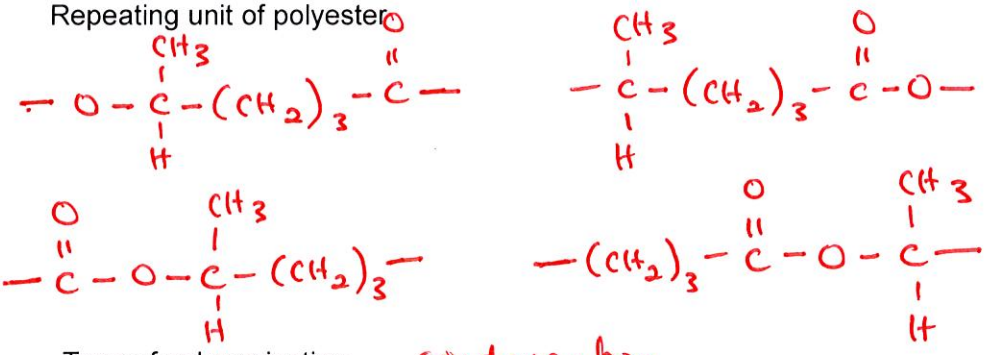
Structure of **T**



M1

Any:

Repeating unit of polyester

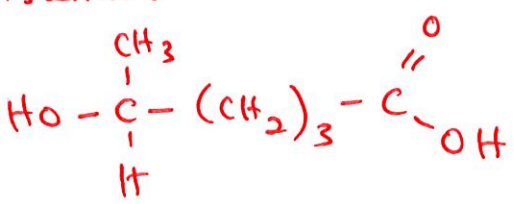


M2

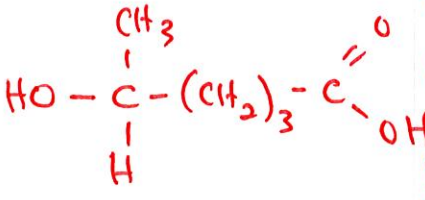
Type of polymerisation condensation

M3

Polymerisation:

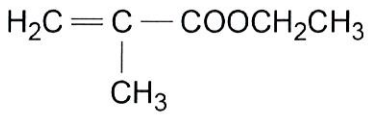


+



Not needed given to show monomers reacting

1 0 . 7 Isomer **U** is shown.



U

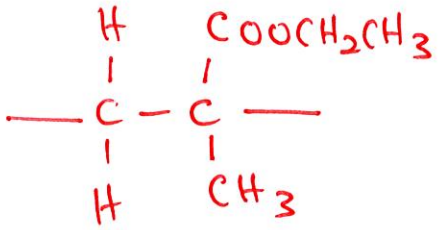
The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in Question **10.6** both contain ester groups that can be hydrolysed.

Draw the repeating unit of the polymer formed by **U**.

Justify the statement that, although both polymer structures contain ester groups, the polymer formed by **U** is not biodegradable.

[3 marks]

Repeating unit of polymer formed by **U**.



M1

Justification

- Non-polar C-C chain M2
- Can't be hydrolysed / attacked by acids / nucleophiles M3

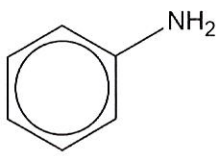
OR

- Only polar ester group M2
- can be hydrolysed / attacked by acids / nucleophiles M3

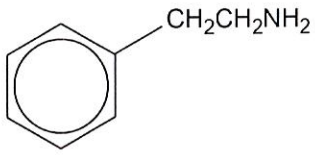
21

Turn over for the next question

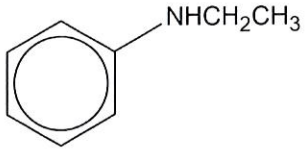
1 1 This question is about the three amines, **E**, **F** and **G**.



E



F



G

1 1 . 1 Amines **E**, **F** and **G** are weak bases.

Explain the difference in base strength of the three amines and give the order of increasing base strength.

[6 marks]

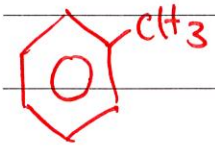
- Order of increasing base strength: M1
  E < G < F
- Base strength is due to availability of lone pair of electrons on nitrogen M2
- E has the lone pair of electrons delocalised M3
  into the benzene ring
- so they are less available to accept H+ M4
- F + G both have alkyl groups next to the M5
  nitrogen which has a positive inductive
  effect towards the nitrogen
- so the lone pair of electrons are more M6
  available to accept H+

1 1 . 2 Amine **F** can be prepared in a three-step synthesis starting from methylbenzene.

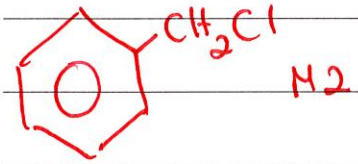
Suggest the structures of the two intermediate compounds.

For each step, give reagents and conditions only. Equations and mechanisms are **not** required.

[5 marks]

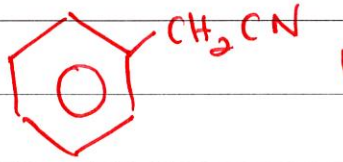


① Cl_2 ↓ UV M1



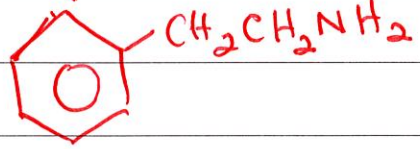
M2

② KCN ↓ alcoholic and aqueous M3



M4

③ H_2 ↓ Ni M5



END OF QUESTIONS

11