

Please write clearly in block capitals.

Centre number

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Candidate number

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Surname

StemUp Model Solution

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	
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10	
11	
TOTAL	



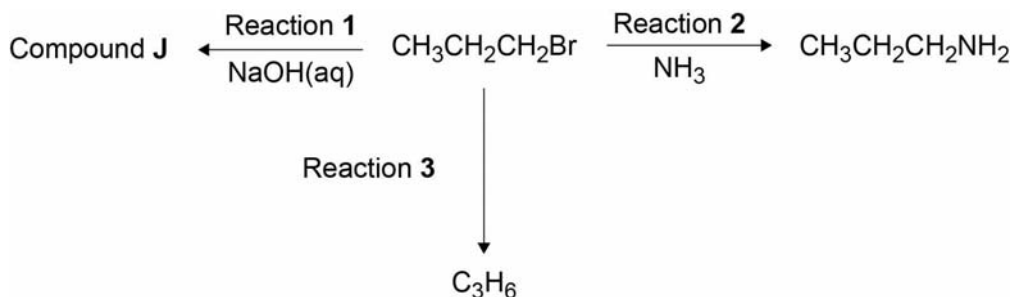
J U N 1 7 7 4 0 5 2 0 1

Answer **all** questions in the spaces provided

0 1

Figure 1 shows some compounds made from a halogenoalkane.

Figure 1

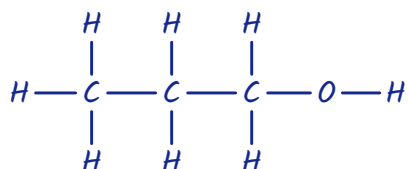


0 1

. 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 $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ is the major product.

[2 marks]

Name of mechanism Nucleophilic substitution

Condition Excess ammonia (NH_3)

0 1

. 3

Calculate the mass, in grams, of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ produced from 25.2 g of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ in Reaction 2 assuming a 75.0% yield.

Give your answer to the appropriate number of significant figures.

[3 marks]

$$n(\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}) = 25.2 \div 122.9 = 0.2050 \text{ mol}$$

$$n(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2) = 0.2050 \times 0.750 = 0.1538 \text{ mol}$$

$$M_r(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2) = 59.0$$

$$\text{mass} = 0.1538 \times 59.0 = 9.07 \text{ g (3 s.f.)}$$

Mass 9.07 g



0 1 . 4

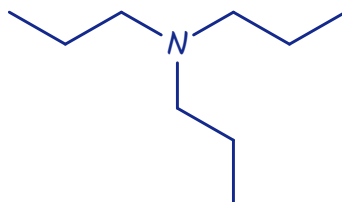
When Reaction 2 is carried out under different conditions, a compound with molecular formula $C_9H_{21}N$ is produced.

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 Tertiary amine (3° amine)

0 1 . 5

Identify the reagent and conditions used in Reaction 3.

[1 mark]

NaOH dissolved in ethanol (ethanolic NaOH), heat

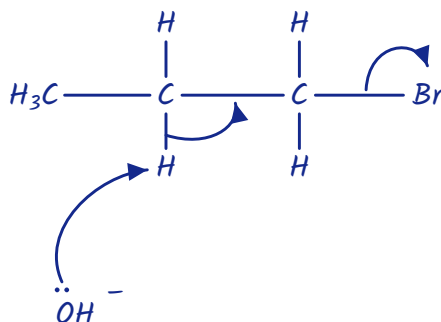
0 1 . 6

Name and outline a mechanism for Reaction 3.

[4 marks]

Name of mechanism (Base) elimination

Mechanism



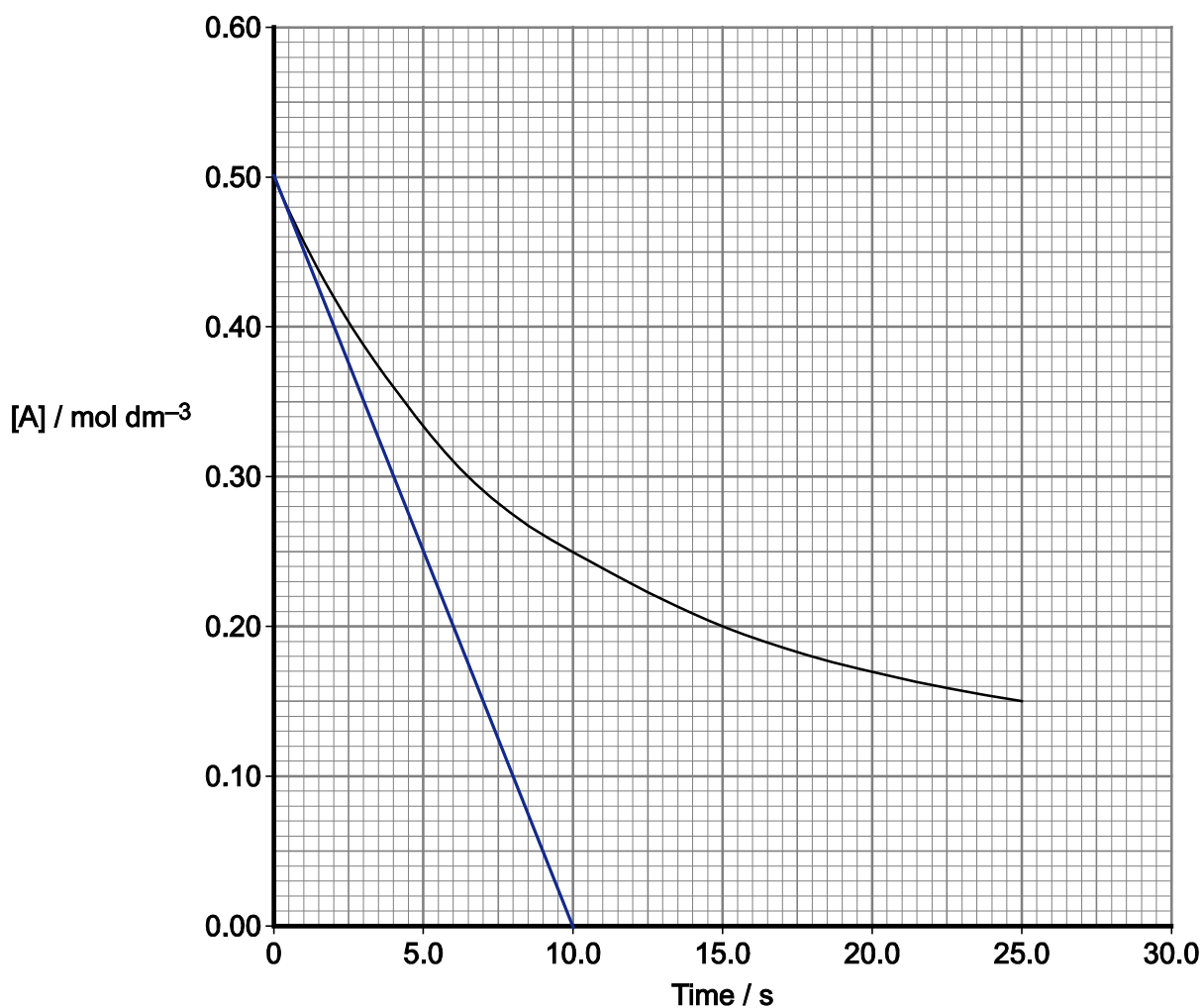
0 2

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

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

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]

$$\text{gradient} = 0.50 \div 10.0 = 0.050$$

Initial rate 0.050 mol dm⁻³s⁻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 $\propto [A]^2$, so $[A]^2$ must increase by a factor of 1.7

$$\text{new } [A]^2 = 1.7 \times (0.50)^2 = 0.425$$

$$\text{new } [A] = \sqrt{0.425} = 0.50 \times \sqrt{1.7} = 0.652$$

Initial concentration of **A** 0.65 mol dm⁻³

4

Turn over for the next question



0	3
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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

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

In one experiment at 25 °C, the initial rate of reaction is $3.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ 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
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Calculate a value for the rate constant at this temperature and give its units.

[3 marks]

$$k = \text{rate} \div ([\text{C}][\text{D}])$$

$$k = 3.1 \times 10^{-3} \div (0.48 \times 0.23)$$

$$k = 2.81 \times 10^{-2}$$

$$\text{units} = \text{mol dm}^{-3} \text{ s}^{-1} \div (\text{mol dm}^{-3})^2$$

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



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 $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

(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]

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

$$E_a = RT(\ln A - \ln k)$$

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

$$E_a = 8.31 \times 298 \times 20.48 = 50\,716 \text{ J mol}^{-1}$$

$$E_a = 50.7 \text{ kJ mol}^{-1} \approx 51 \text{ kJ mol}^{-1}$$

Activation energy 51 kJ mol^{-1}



0	4
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The aldehyde $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ reacts with KCN followed by dilute acid to form a racemic mixture of the two stereoisomers of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CN}$

0	4	.	1
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Give the IUPAC name of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CN}$

[1 mark]

2-hydroxyhexanenitrile

0	4	.	2
---	---	---	---

Describe how you would distinguish between separate samples of the two stereoisomers of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CN}$

[2 marks]

Pass plane-polarised light through each sample (in a polarimeter).

The two enantiomers rotate the plane of plane-polarised light by the same angle but in opposite directions (one clockwise, one anticlockwise).

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

[3 marks]

The carbonyl group ($\text{C}=\text{O}$) in the aldehyde is planar.

The nucleophile $:\text{CN}^-$ can attack the carbonyl carbon from either side of the plane (above or below) with equal probability.

So equal amounts of the two enantiomers are produced, giving a racemic mixture.



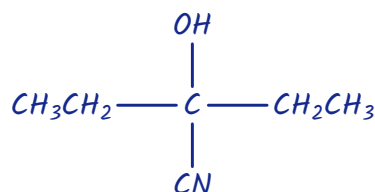
0 4 . 4

An isomer of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ 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

It has no chiral centre: the central C is attached to two identical ethyl groups, so not to 4 different groups.

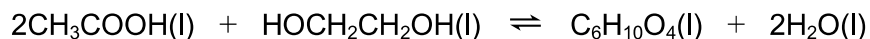
8

Turn over for the next question



0 5

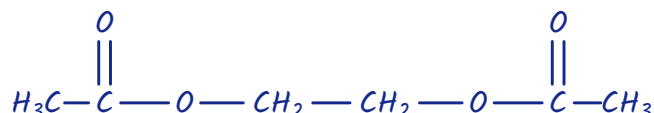
Ethanoic acid and ethane-1,2-diol react together to form the diester ($\text{C}_6\text{H}_{10}\text{O}_4$) as shown.



0 5 . 1

Draw a structural formula for the diester $\text{C}_6\text{H}_{10}\text{O}_4$

[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	$\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{C}_6\text{H}_{10}\text{O}_4$	H_2O
At the start	0.470	0.205	0	0
At equilibrium	0.180	0.060	0.145	0.290

[3 marks]

Space for working

$$\text{CH}_3\text{COOH reacted} = 0.470 - 0.180 = 0.290 \text{ mol}$$

$$\text{diol reacted} = 0.290 \div 2 = 0.145 \text{ mol}$$

$$\text{diol left} = 0.205 - 0.145 = 0.060 \text{ mol}$$

$$\text{C}_6\text{H}_{10}\text{O}_4 \text{ formed} = 0.145 \text{ mol} ; \text{H}_2\text{O formed} = 2 \times 0.145 = 0.290 \text{ mol}$$



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

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

Justification Equal numbers of moles on each side (3 and 3), so the volume V cancels out in the K_c expression.

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 ₃ COOH	HOCH ₂ CH ₂ OH	C ₆ H ₁₀ O ₄	H ₂ O
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]

$$V \text{ cancels, so } K_c = (0.802 \times 1.15^2) \div (n^2 \times 0.264)$$

$$n(CH_3COOH)^2 = (0.802 \times 1.15^2) \div (6.45 \times 0.264)$$

$$= 1.0606 \div 1.7028 = 0.623$$

$$n(CH_3COOH) = \sqrt{0.623} = 0.789 \text{ mol}$$

Amount of ethanoic acid 0.789 mol

9



0 6

Use the Data Booklet to help you answer this question.

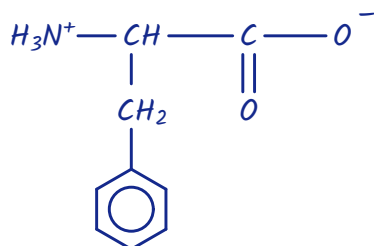
This question is about amino acids and peptide (amide) links.

0 6

. 1

Draw the structure of the zwitterion formed by phenylalanine.

[1 mark]

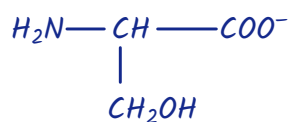


0 6

. 2

Draw the structure of serine at high pH.

[1 mark]



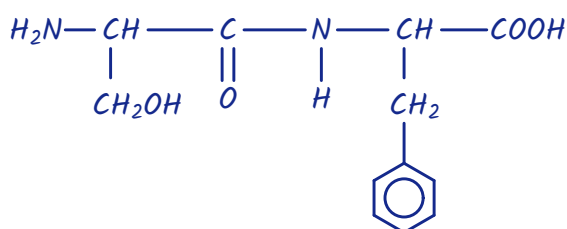
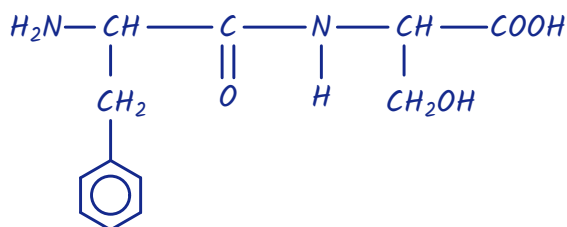
0 6

. 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]



0 6 . 4

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

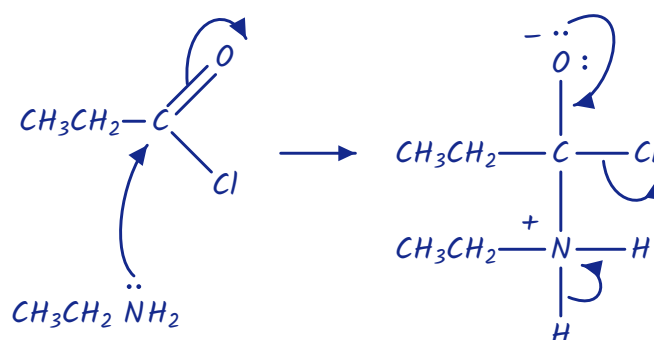
Name and outline a mechanism for the reaction between $\text{CH}_3\text{CH}_2\text{COCl}$ and $\text{CH}_3\text{CH}_2\text{NH}_2$

Give the IUPAC name of the organic product.

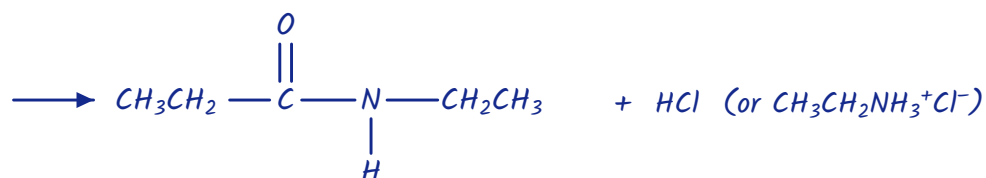
[6 marks]

Name of mechanism Nucleophilic addition-elimination

Mechanism



(H^+ removed by a second $\text{CH}_3\text{CH}_2\text{NH}_2$)



IUPAC name of organic product N-ethylpropanamide

10



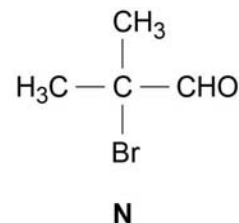
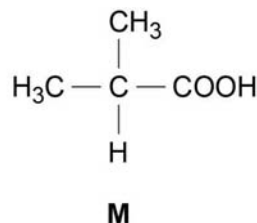
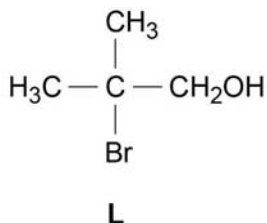
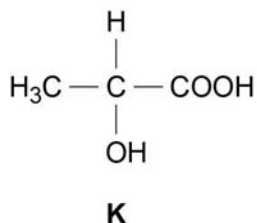
0 7

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.



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.

[6 marks]

Test 1 (on all four): add sodium hydrogencarbonate solution,

$\text{NaHCO}_3(\text{aq})$. K and M (carboxylic acids) give effervescence and

the gas (CO_2) turns limewater milky. L and N show no change

(no fizzing).

Test 2 on K and M: warm with acidified potassium

dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$. K (a secondary alcohol) turns the

solution from orange to green. M has no alcohol group, so it stays

orange.

Test 2 on L and N: warm with Tollens' reagent. N (an aldehyde)

gives a silver mirror. L (a primary alcohol, no aldehyde) gives no

change, the solution stays colourless.

So all four compounds are identified using only two tests on each.



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]



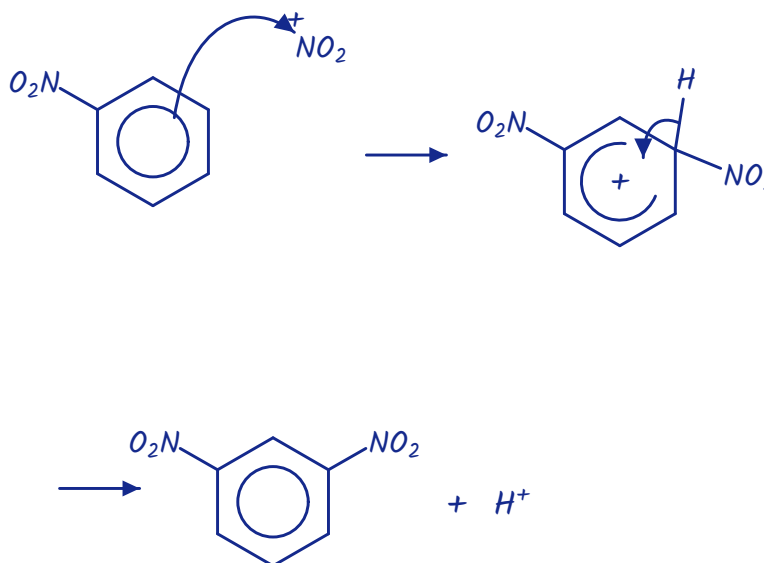
0 8 . 2

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

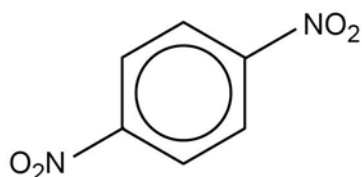
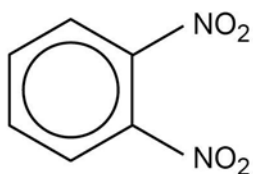


Turn over for the next question



0 8 . 3

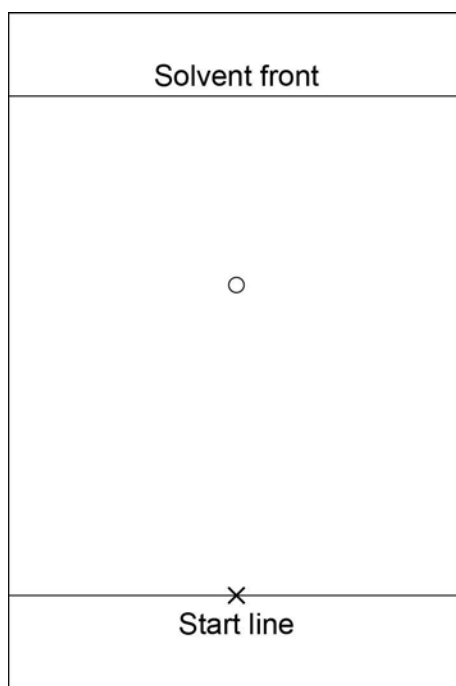
The dinitrobenzenes shown were investigated by thin layer chromatography (TLC).



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.

[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]

*The balance between its solubility in the moving (mobile) phase,
the solvent, and its retention by (attraction to) the stationary
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]

The solvent level in the beaker 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; 1,4- is non-polar

Explanation

*1,4-dinitrobenzene is non-polar, so it is less attracted to the polar
stationary phase (plate) and more soluble in the non-polar hexane,
so it moves further.*



08.7

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 the solvent is more polar than hexane alone.

The polar 1,2-dinitrobenzene is more attracted to / more soluble in this solvent than before, so it travels further and its R_f is greater.

12



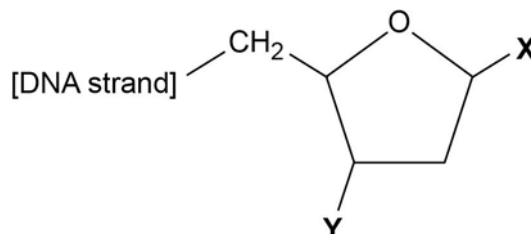
0 9

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 A (nitrogenous) base, e.g. adenine

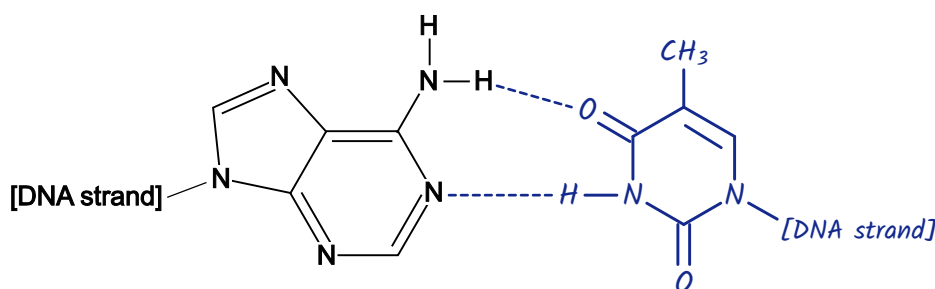
Y A phosphate group

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.

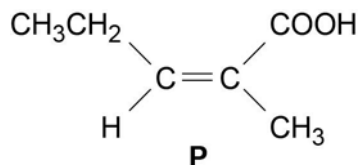
[2 marks]



1 0

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

1 0 . 1

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

[1 mark]

(2)-2-methylpent-2-enoic acid

1 0 . 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

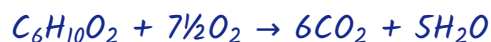
When this gas mixture was passed through aqueous sodium hydroxide, the carbon dioxide reacted and the volume of gas decreased to 155 cm^3

Both gas volumes were measured at 25°C and 105 kPa

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 $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

[5 marks]



$$V(CO_2) = 335 - 155 = 180 \text{ cm}^3 = 180 \times 10^{-6} \text{ m}^3$$

$$n(CO_2) = pV \div RT = (105\,000 \times 180 \times 10^{-6}) \div (8.31 \times 298)$$

$$n(CO_2) = 7.632 \times 10^{-3} \text{ mol}$$

$$n(P) = 7.632 \times 10^{-3} \div 6 = 1.272 \times 10^{-3} \text{ mol}$$

$$M_r(C_6H_{10}O_2) = 114.0$$

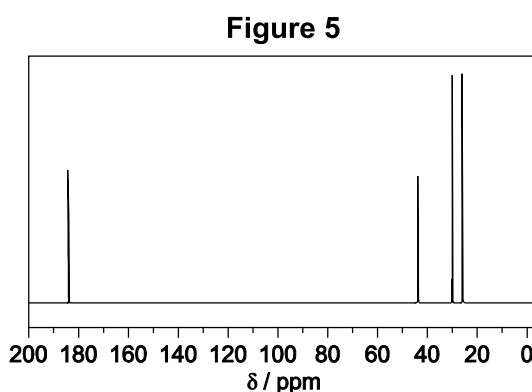
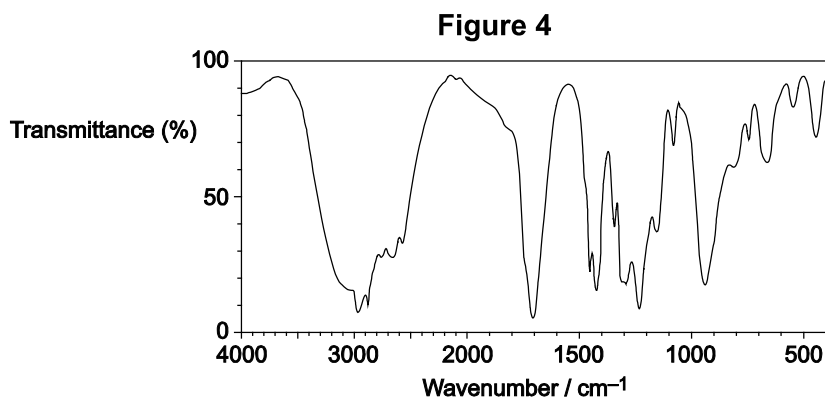
$$\text{mass} = 1.272 \times 10^{-3} \times 114.0 = 0.145 \text{ g} = 145 \text{ mg}$$

Mass of **P** used 145 mg



1 0 . 3

Isomer **Q** ($\text{C}_6\text{H}_{10}\text{O}_2$) 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**.

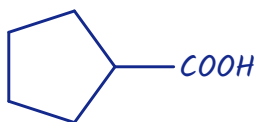


Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.

In your answer, state one piece of evidence you have used from each spectrum.

[3 marks]

Structure of **Q**.



Evidence from **Figure 4**

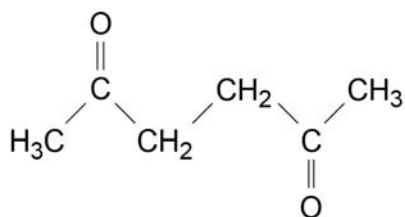
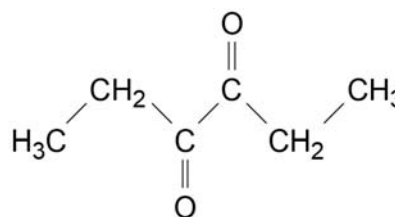
Broad O-H (acid) absorption at 2500 to 3000 cm^{-1} , so a
carboxylic acid ($\text{C}=\text{O}$ at about 1700 cm^{-1}).

Evidence from **Figure 5**

4 peaks, so 4 carbon environments; peak at about 180 ppm (160
to 185) shows $\text{C}=\text{O}$ of an acid.



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 atoms next to a C=O (2 CH₃ and 2 CH₂); S has only 2 (the CH₂ groups).

So R has two peaks in the range δ 20 to 50 (C-C=O), S only one; the CH₃ of S gives a lower peak (δ 5 to 40).

Number of peaks *R: 3 peaks; S: 3 peaks (both have three)*



1	0
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Although the ^1H 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: both peaks are singlets (CH_3 and the equivalent CH_2 groups, δ

2.1 to 2.6, have no H on adjacent C).

S: CH_3 peak (δ 0.7 to 1.2) is a triplet; CH_2 peak (δ 2.1 to 2.6) is a quartet.

Number of peaks *R: 2 peaks; S: 2 peaks (both have two)*

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** ($C_6H_{10}O_2$).

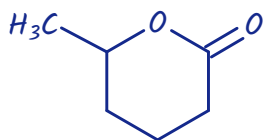
Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

Draw the structure of **T**.

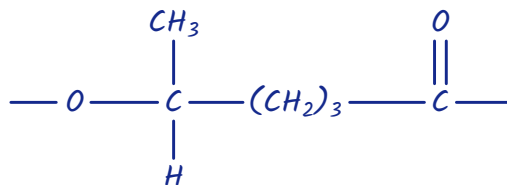
Draw the repeating unit of the polyester and name the type of polymerisation.

[3 marks]

Structure of **T**



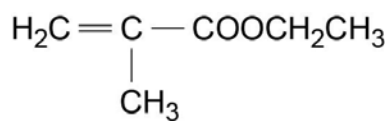
Repeating unit of polyester



Type of polymerisation Condensation (polymerisation)



1 0 . 7

Isomer **U** is shown.**U**

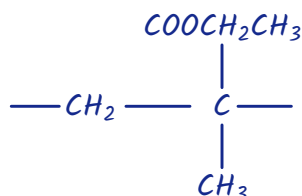
The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in Question 10.6 both contain ester groups that can be hydrolysed.

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**.



Justification

The main chain contains only strong, non-polar C-C bonds, which cannot be attacked by nucleophiles, so cannot be hydrolysed.

The polar ester group is only in the side chain, so even if it is hydrolysed the polymer chain is not broken.

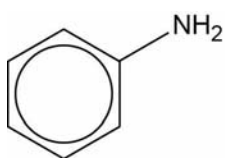
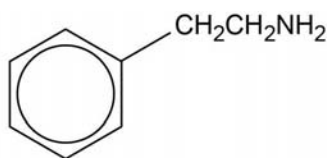
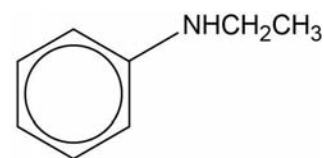
21

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]

Base strength depends on the availability of the lone pair of electrons on the N atom to accept a proton (H^+).

In E, the N is bonded directly to the benzene ring, so its lone pair is delocalised into the ring. The lone pair is much less available to accept H^+ , so E is the weakest base.

In F, the N is attached to an alkyl group (CH_2CH_2), not to the ring. The alkyl group has a positive inductive effect, pushing electrons towards the N, so the lone pair is more available to accept H^+ . F is the strongest base.

In G, the N is attached to an ethyl group, which pushes electrons onto the N (inductive effect), but the N is also bonded to the ring, so its lone pair is partly delocalised into the ring. So G is a stronger base than E but weaker than F.

Order of increasing base strength: $E < G < F$



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]

Step 1: methylbenzene is converted to (chloromethyl)benzene,

$C_6H_5CH_2Cl$ (intermediate 1).

Reagents and conditions: chlorine, Cl_2 , with UV light.

Step 2: $C_6H_5CH_2Cl$ is converted to phenylethanenitrile, $C_6H_5CH_2CN$

(intermediate 2).

Reagents and conditions: KCN in aqueous ethanol (both ethanol and water), heat under reflux.

Step 3: $C_6H_5CH_2CN$ is reduced to amine F, $C_6H_5CH_2CH_2NH_2$.

Reagents and conditions: hydrogen, H_2 , with a nickel catalyst.

END OF QUESTIONS

11



There are no questions printed on this page

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