AQA

Please write clearly in block capitals.

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

Surname _____

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	

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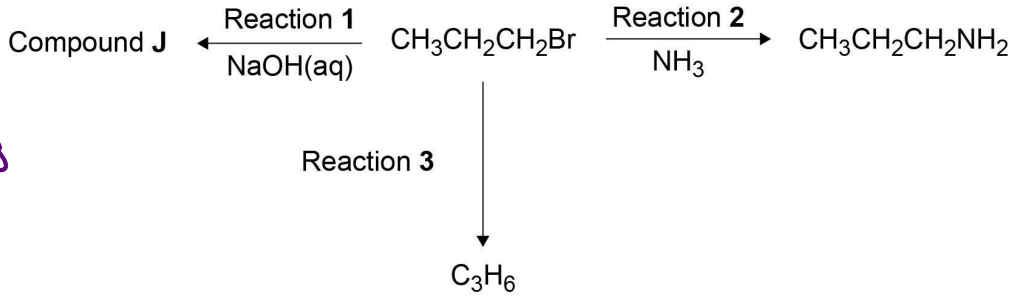
Answer **all** questions in the spaces provided

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

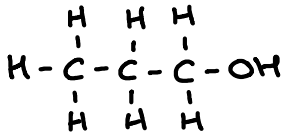
Figure 1



Replacing Br with OH

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]

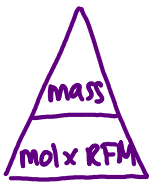
Name of mechanism Nucleophilic substitution

Condition Excess NH_3 (ensures 1° product produced)

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]



M_r of $CH_3CH_2CH_2Br$ = 12 + 3 + 12 + 2 + 12 + 2 + 79.9 = 122.9 $g\,mol^{-1}$

$\frac{25.2}{122.9} = 0.205$ mol As assuming 75% yield

$0.205 \times 0.75 = 0.154$ mol

$0.154 \times 59 = 9.07$ g

↳ M_r of $CH_3CH_2CH_2NH_2$

12+3+12+2+12+2+14+2 = 59

Mass 9.07 g

Do not write outside the box

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.

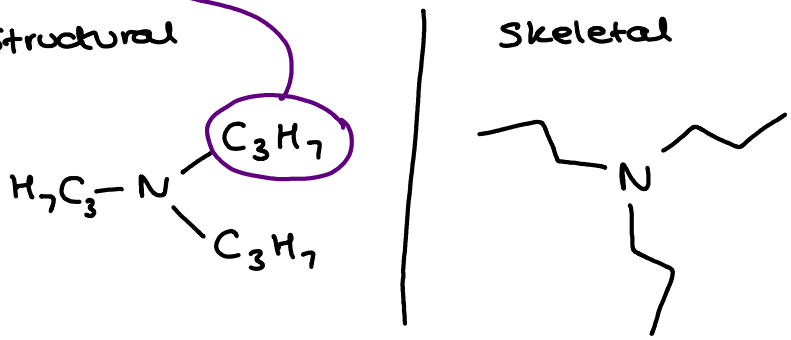
Identify the functional group in the compound including its classification.

[2 marks]

Propyl groups

Skeletal formula

Structural



Skeletal

Functional group including classification tertiary amine

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

[1 mark]

NaOH and Ethanolic

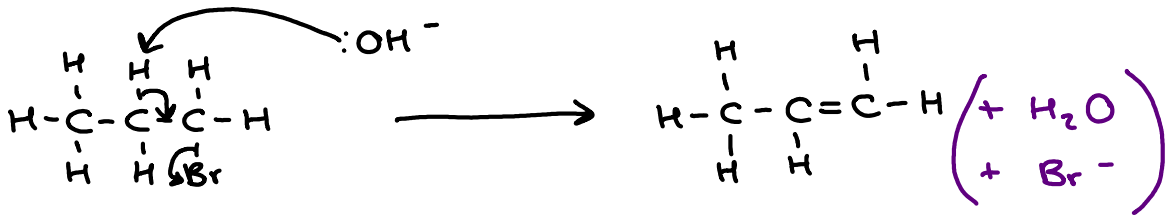
0 1 . 6 Name and outline a mechanism for Reaction **3**.

[4 marks]

Elimination as alkene produced

Name of mechanism Elimination

Mechanism



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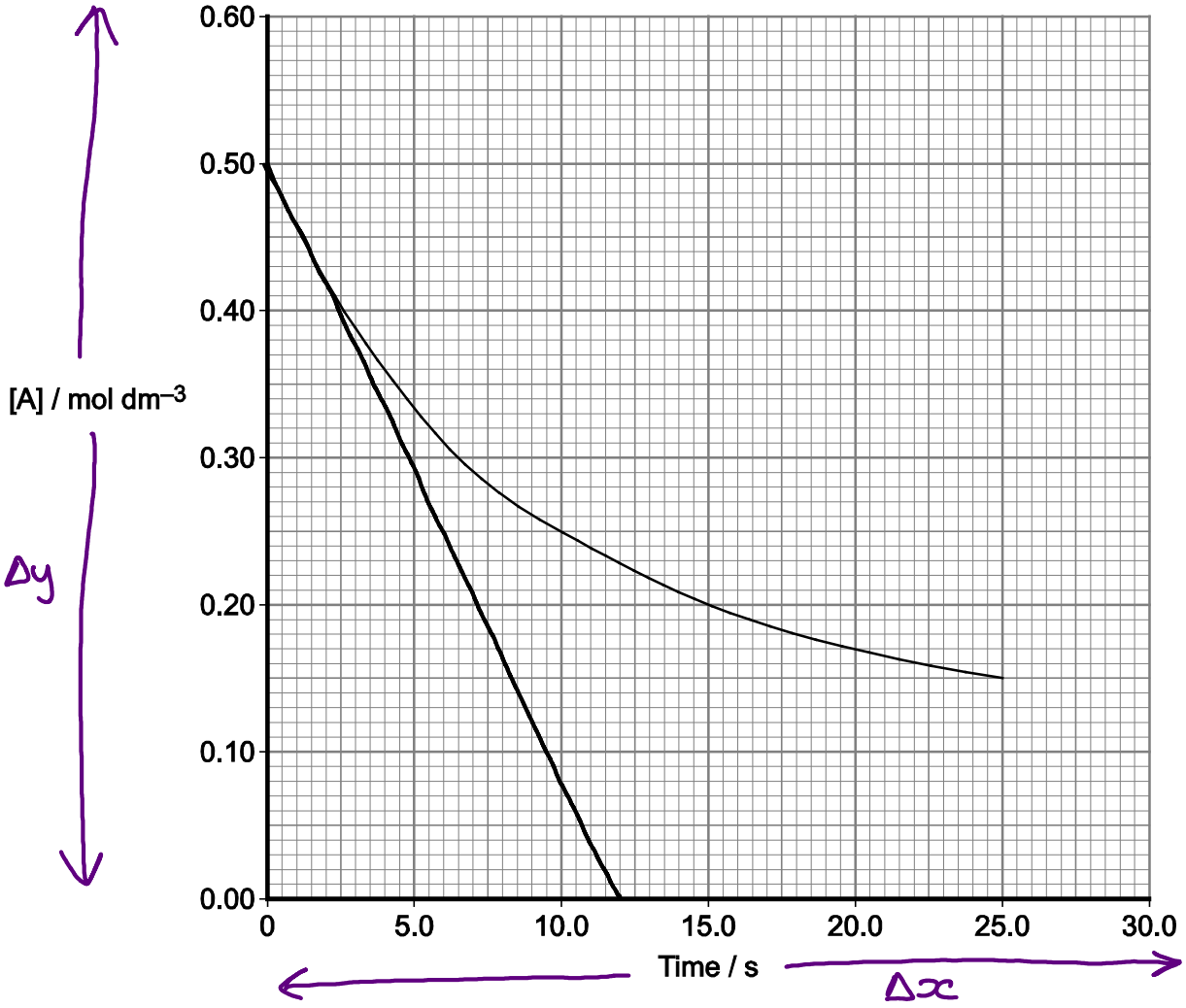
0 2 The rate equation for the reaction between compounds **A** and **B** is

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

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]

Tangent ⇒ Gradient = Rate of Reaction

$$\frac{\Delta y}{\Delta x} = \frac{0.5}{12} = 0.416$$

Initial rate 0.416 mol $dm^{-3}s^{-1}$

Do not write outside the box

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]

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

$\text{Rate} = k[A]^2[B]$ (Reaction 1)

$\text{Rate} = k[A]^2[B]$ (Reaction 2)

$$1.7 = \frac{k[A]^2[B]}{k[0.5]^2[B]} = \frac{[A]^2}{[0.5]^2}$$

$[A]^2 = 1.7 \times [0.5]^2 = 0.425$

$[A] = 0.65$

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

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]

Rate = k [C][D]

Rearrange for k by ÷ by [C][D]

$3.1 \times 10^{-3} = k[0.48][0.23]$

$k = \frac{3.1 \times 10^{-3}}{[0.48][0.23]} = 2.8 \times 10^{-2}$

Units: $\frac{\text{mol dm}^{-3}\ s^{-1}}{\text{mol dm}^{-3}\ \text{mol dm}^{-3}} = \frac{s^{-1}}{\text{mol dm}^{-3}} = \text{mol}^{-1}\ dm^3\ s^{-1}$

when we flip the indices if +ve becomes -ve and vice versa

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

Do not write outside the box

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

Arrhenius Equation

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

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 $\ln A = 16.9$

273+25 = 298 K → Convert into kelvin as units = JK^{-1}mol^{-1}

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]

our value is 2.8×10^{-2}

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

$$\ln(2.8 \times 10^{-2}) = \frac{-Ea}{8.31 \times 298} + 16.9$$ → -16.9 from both sides

$$-3.5727 - 16.9 = \frac{-Ea}{2476.38}$$

store full answer on calculator don't round

$$-20.4727 \times 2476.38 = -Ea$$

$$-50,716 \text{ J mol}^{-1} = -Ea$$

$$50.716 \text{ kJ mol}^{-1} = Ea$$

$$51 \text{ kJ mol}^{-1} = Ea$$

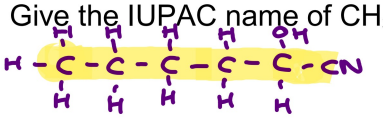
Activation energy 51 kJ mol^{-1}

7

Do not write outside the box

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 $CH_3CH_2CH_2CH_2CH(OH)CN$



6 C chain OH and CN functional group

[1 mark]

2 hydroxyhexanenitrile

nitrile — priority

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]

Using a polarising filter as we have compounds that are optically active (as chiral carbons allow the group to be arranged differently known as enantiomers).

- plane polarized light
- Enantiomers would rotate light in opposite directions

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

[3 marks]

Functional group of an aldehyde is C=O which is a carbonyl group that is planar. Thus the planar molecule has a 50 : 50 chance of being attatched from either side.

Do not write outside the box

nucleophilic addition

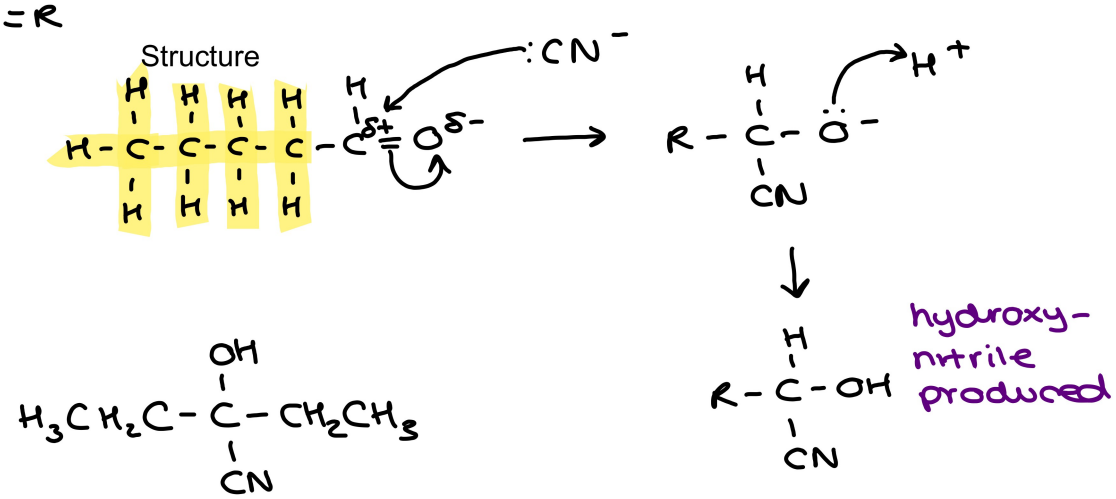
0 4 . 4 An isomer of $CH_3CH_2CH_2CH_2CHO$ reacts with KCN followed by dilute acid to form a compound that does not show stereoisomerism.

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

[2 marks]

= R

Structure



Justification

As 2 ethyl groups (CH_2CH_3) no chiral carbon.

Structural isomerism: Same molecular formula but different structural formula.

8

Turn over for the next question

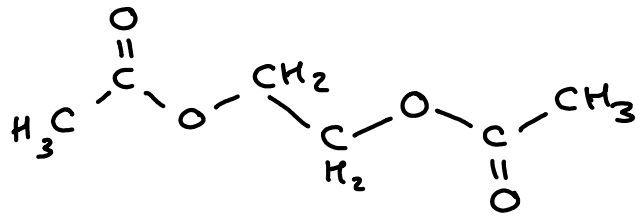
Do not write outside the box

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**.

Same molar ratio so change is the same

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	0.06	0.145	0.290

[3 marks]

Space for working

$0.470 - 0.180 = 0.290$ mol

$\frac{0.290}{2} = 0.145$ mol

$0.205 - 0.145 = 0.06$ 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 $K_c = \dfrac{[\text{ester}] \times [H_2O]^2}{[CH_3COOH]^2 \times [HOCH_2CH_2OH]}$

Justification volume cancels out OR equal number of moles on each side.

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]

$$6.45 = \frac{(8.02 \times 10^{-1}/V)(1.15/V)^2}{[CH_3COOH]^2 (2.64 \times 10^{-1}/V)}$$

As volume cancels out ...

$$\frac{0.802 \times 1.15^2}{6.45 \times 0.264} = [CH_3COOH]^2 \text{ (mol)}$$

$$\sqrt{\frac{0.802 \times 1.15^2}{6.45 \times 0.264}} = \sqrt{0.623} = 0.789 \text{ mol}$$

Amount of ethanoic acid 0.789 mol

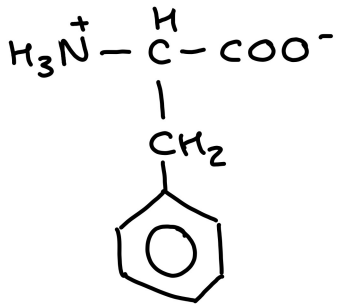
9

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.

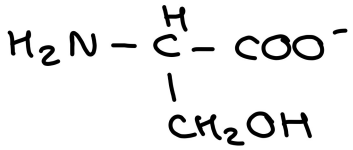
[1 mark]



positively and negatively charged NH_2 and COOH groups

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

[1 mark]

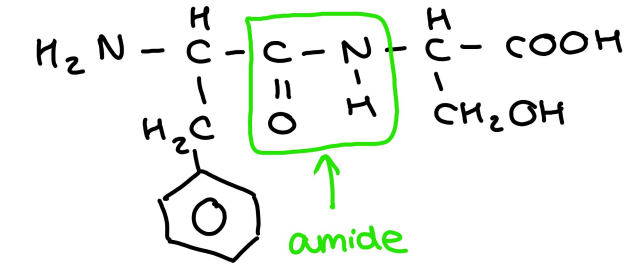


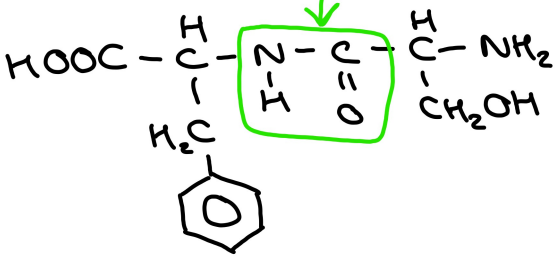
alkaline deprotonates carboxylic acid group.

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]





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

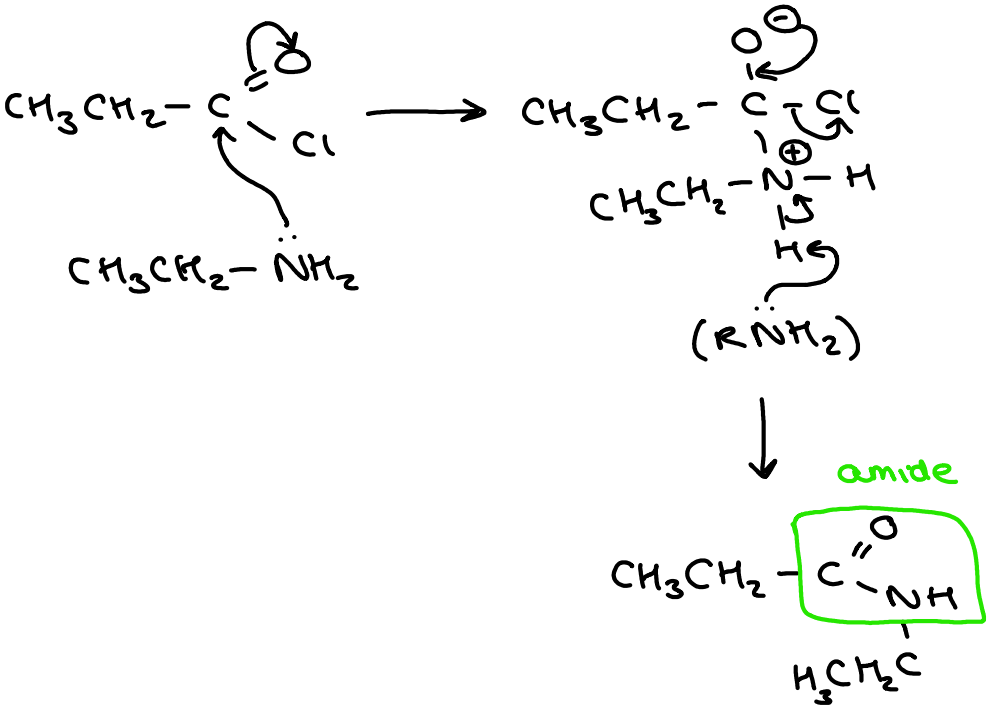
Name and outline a mechanism for the reaction between CH_3CH_2COCl and $CH_3CH_2NH_2$

Give the IUPAC name of the organic product.

[6 marks]

Name of mechanism nucleophilic addition - elimination

Mechanism



IUPAC name of organic product N-ethylpropanamide

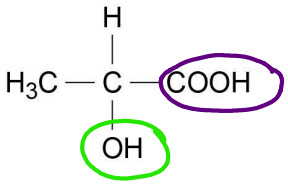
10

Do not write outside the box

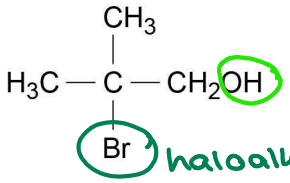
0 7 Test-tube reactions can be used to identify the functional groups in organic molecules.

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

carboxylic acid



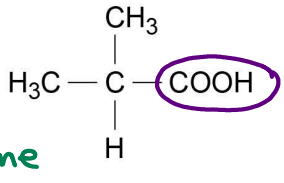
K



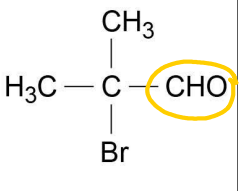
L

haloalkane

aldehyde



M



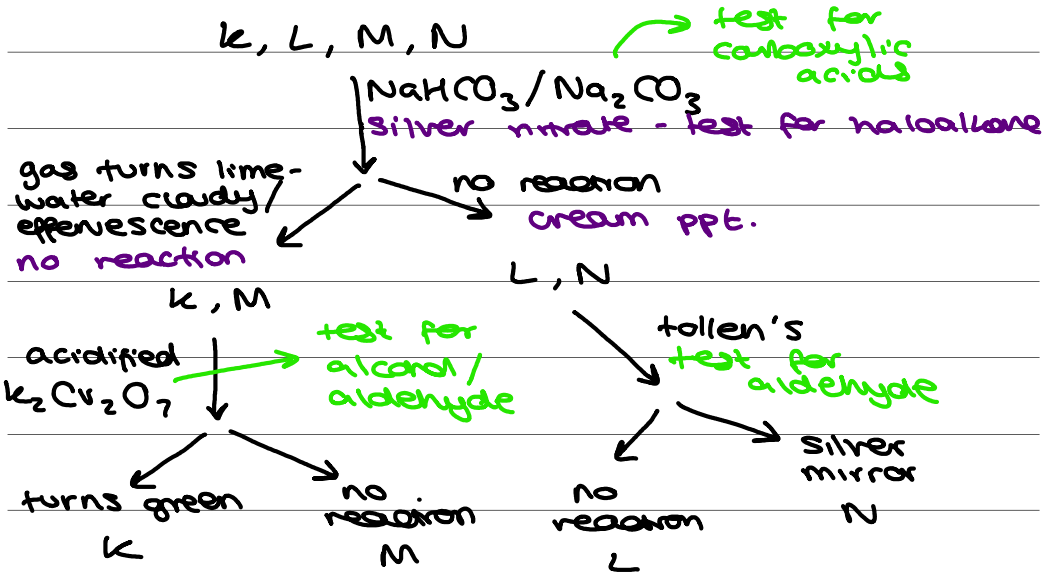
N

alcohol

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]



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.

need an electrophile

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

[1 mark]

electrophile

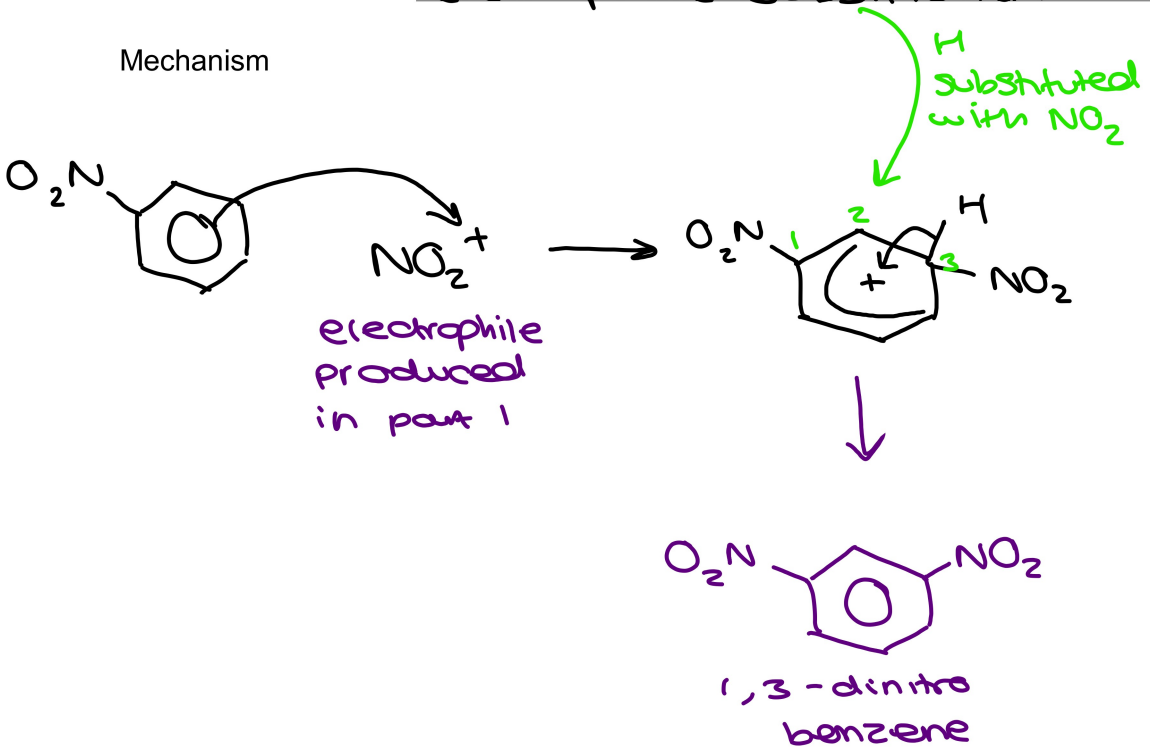
$$HNO_3 + 2H_2SO_4 \longrightarrow \boxed{NO_2^+} + H_3O^+ + 2HSO_4^-$$

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

[4 marks]

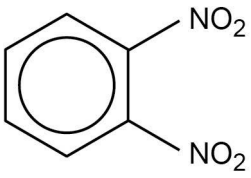
Name of mechanism electrophilic substitution

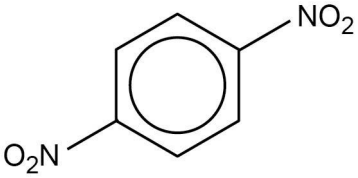
Mechanism



Turn over for the next question

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



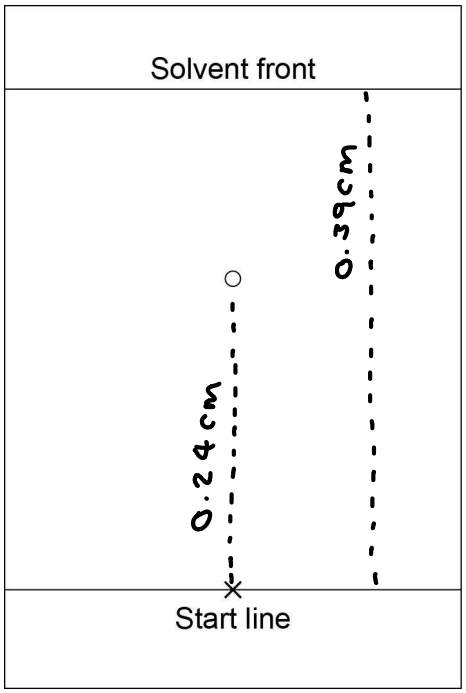


In an experiment, carried out in a fume cupboard, a concentrated solution of pure 1,4-dinitrobenzene was spotted on a TLC plate coated with a solid that contains polar bonds. Hexane was used as the solvent in a beaker with a lid.

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**

$R_f = \frac{\text{distance moved by sample}}{\text{solvent front}}$

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]

$\frac{0.24}{0.39} = 0.62$

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]

Solubility in moving phase and retention by 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]

Solvent depth 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]

↳ distance travelled by sample is greater

Relative polarities

1,2-dinitrobenzene is more polar

Explanation

1,4-dinitrobenzene is less attracted to stationary phase.

Do not write outside the box

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]

Solvent more polar so the polar isomer is more attracted to the solvent.

So sample will more further up / distance travelled by sample will be greater.

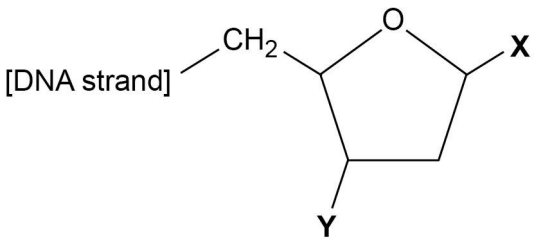
12

Do not write outside the box

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

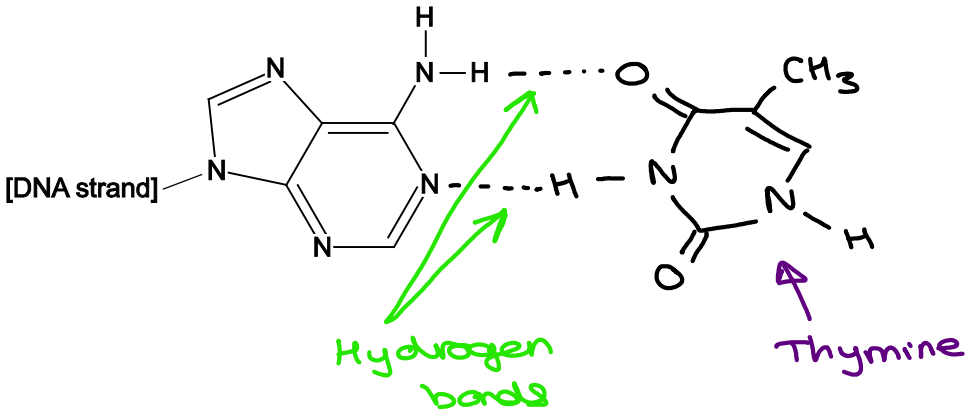
Y phosphate group

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]

DNA pairs AT, GC



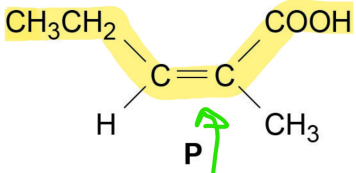
4

Do not write outside the box

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**.

longest carbon chain pent...



alkene

[1 mark]

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

[5 marks]

$$C_6H_{10}O_2 + 7\tfrac{1}{2}O_2 \longrightarrow 6CO_2 + 5H_2O$$

volume of CO_2: $335 - 155 = 180\ cm^3$

$PV = nRT \longrightarrow n = PV/RT$

moles of CO_2: $\dfrac{105000\ Pa \times (180 \times 10^{-6})\ m^3}{8.31\ J K^{-1} mol^{-1} \times (273 + 25)\ K}$

$= 7.632 \times 10^{-3}$ mol

moles of P: $7.632 \times 10^{-3} \div 6 = 1.272 \times 10^{-3}$ mol

mass of P: $1.272 \times 10^{-3} \times ((6 \times 12) + 10 + (16 \times 2))$

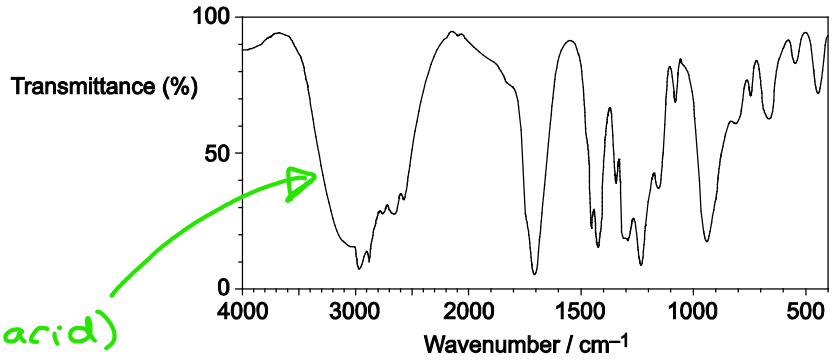
$= 145\ mg \longrightarrow 0.145\ g$

Mass of **P** used 145 mg

Do not write outside the box

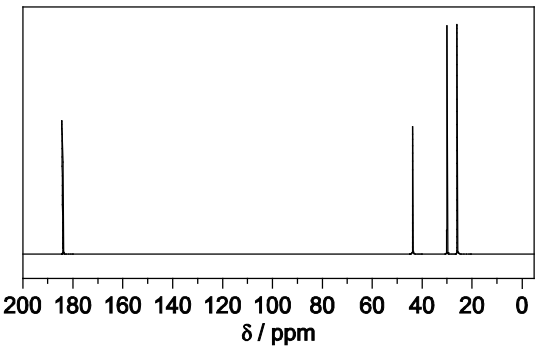
1 0 . 3 Isomer **Q** ($C_6H_{10}O_2$) is a cyclic compound. The infrared spectrum of **Q** is shown in **Figure 4** and the ^{13}C NMR spectrum of **Q** is shown in **Figure 5.**

Figure 4



OH (acid) peak

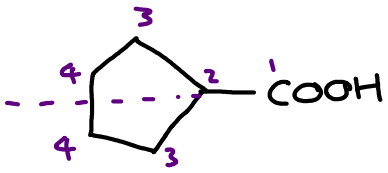
Figure 5

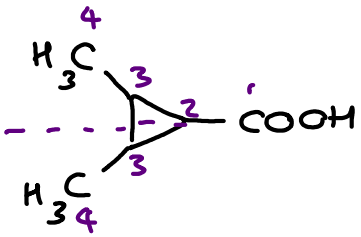


Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.
In your answer, state one piece of evidence you have used from each spectrum.

[3 marks]

Structure of **Q**.





Evidence from **Figure 4**

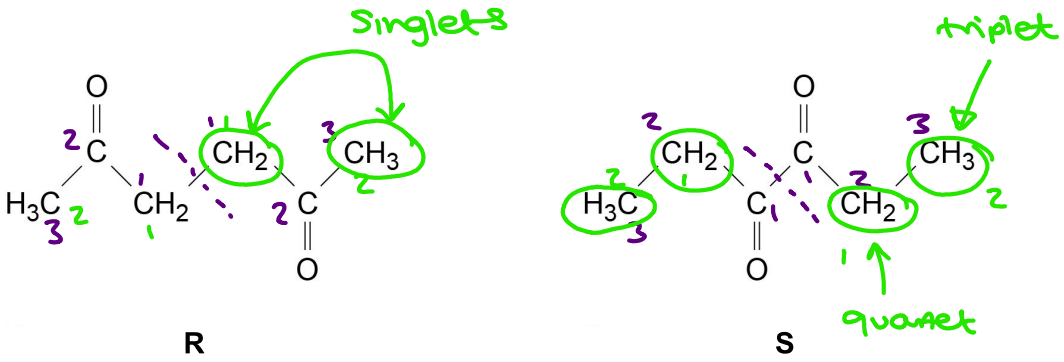
OH (acid) peak 2500 - 3000 cm-1 present

Evidence from **Figure 5**

^{13}C NMR has 4 peaks so 4 environments

Do not write outside the box

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 4C next to C=O
- S has 2C next to C=O
- In the range δ = 20-50 R has 2 peaks and S only has one.

Number of peaks 3

Do not write outside the box

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 both singlets
- S has a triplet and a quartet

Number of peaks 2

Question 10 continues on the next page

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

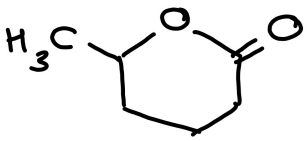
Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

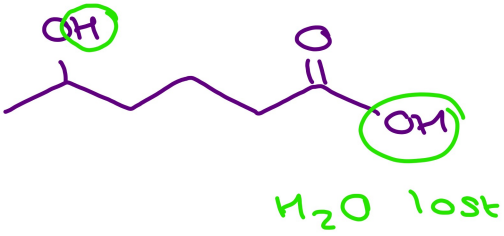
Draw the structure of **T**.

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

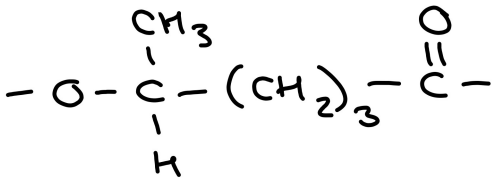
[3 marks]

Structure of **T**





Repeating unit of polyester



Type of polymerisation Condensation

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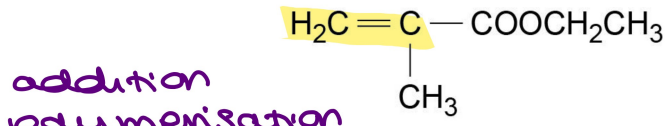
10.7 Isomer **U** is shown.



addition polymerisation

U

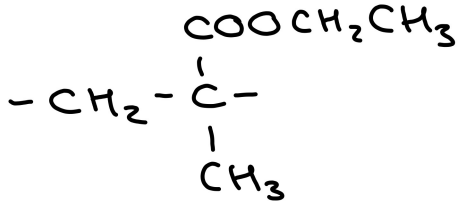
The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in Question **10.6** both contain ester groups that can be hydrolysed.

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

• Strong non-polar C-C bonds cannot be attacked by nucleophiles/ hydrolysed.

21

Turn over for the next question

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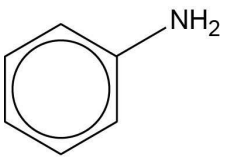
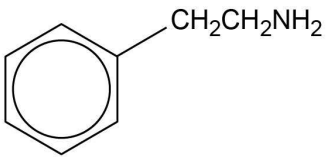
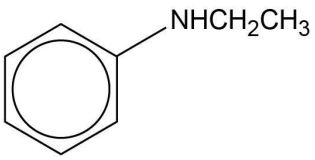
1 1 This question is about the three amines, **E**, **F** and **G**.



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]

Strength depends on availability of lone pair on N

E: N lone pair is delocalised into the ring so is less available to donate / accept H^+

F or G: electrons pushed to N, +I inductive effect so more available to donate / accept H^+

Base strength order: E < G < F

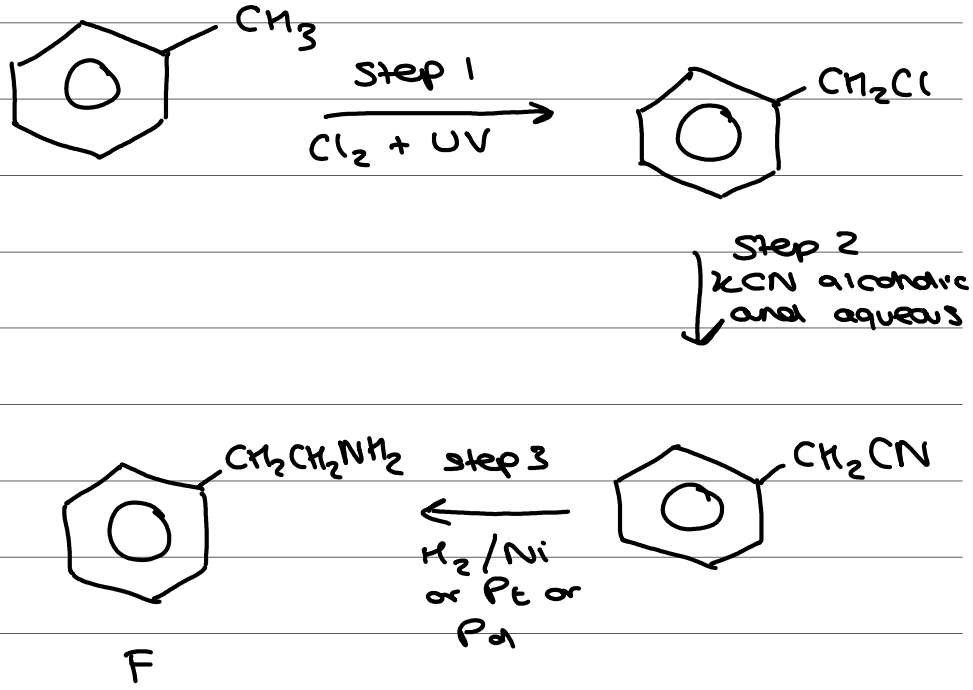
Do not write outside the box

11 . 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]



END OF QUESTIONS

11

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ANSWER IN THE SPACES PROVIDED