

A-level Chemistry (7405/2)

Paper 2: Organic and Physical Chemistry

Specimen 2015 v0.5

Session

2 hours

Materials

For this paper you must have:

- the Data Booklet, provided as an insert
- a ruler
- a calculator.

Instructions

- Answer **all** questions.
- Show **all** your working.

Information

- The maximum mark for this paper is 105.

Please write clearly, in block capitals, to allow character computer recognition.

Centre number

Candidate number

Surname STEMUP MODEL SOLUTION

Forename(s)

Candidate signature _____

Answer **all** questions.

- 1** This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in **Table 1** were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Table 1

Experiment	Initial concentration of A / mol dm ⁻³	Initial concentration of B / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.12	0.26	2.10×10^{-4}
2	0.36	0.26	1.89×10^{-3}
3	0.72	0.13	3.78×10^{-3}

- 0 1 . 1** Show how these data can be used to deduce the rate expression for the reaction between **A** and **B**.

[3 marks]

Experiments 1 and 2: [B] is constant and [A] increases $\times 3$, and the rate increases $\times 9$ ($= 3^2$), so the reaction is 2nd order with respect to A.

Experiments 2 and 3: [A] increases $\times 2$, so the rate should increase $\times 2^2 = 4$, but it only increases $\times 2$. So halving [B] halves the rate, so it is 1st order with respect to B.

Rate equation: rate = $k[A]^2[B]$

The data in **Table 2** were obtained in two experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Table 2

Experiment	Initial concentration of C / mol dm ⁻³	Initial concentration of D / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
4	1.9×10^{-2}	3.5×10^{-2}	7.2×10^{-4}
5	3.6×10^{-2}	5.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- 0 1** . **2** Use the data from experiment **4** to calculate a value for the rate constant, k , at this temperature. Deduce the units of k .

[3 marks]

$$\text{rate} = k[\text{C}]^2[\text{D}] \text{ so } k = \text{rate} \div [\text{C}]^2[\text{D}]$$

$$k = 7.2 \times 10^{-4} \div ((1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2}))$$

$$k = 7.2 \times 10^{-4} \div 1.2635 \times 10^{-5} = 57.0$$

$$k = \underline{57.0} \quad \text{Units} = \underline{\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}}$$

- 0 1** . **3** Calculate a value for the initial rate in experiment **5**.

[1 mark]

$$\text{rate} = 57.0 \times (3.6 \times 10^{-2})^2 \times (5.4 \times 10^{-2})$$

$$= 3.99 \times 10^{-3}$$

$$\text{Initial rate} = \underline{3.99 \times 10^{-3}} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Question 1 continues on the next page

0 1 . 4 The rate equation for a reaction is

$$\text{rate} = k[\text{E}]$$

Explain qualitatively why doubling the temperature has a much greater effect on the rate of the reaction than doubling the concentration of E.

[3 marks]

A reaction only occurs when colliding molecules have energy greater than or equal to the activation energy ($E \geq E_a$).

Doubling the temperature causes many more molecules to have this energy (far more molecules in the Maxwell-Boltzmann distribution have $E \geq E_a$).

Whereas doubling $[E]$ only doubles the number of molecules with this energy, so the rate only doubles.

0 1 . 5 A slow reaction has a rate constant $k = 6.51 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3$ at 300 K.

Use the equation $\ln k = \ln A - E_a/RT$ to calculate a value, in kJ mol^{-1} , for the activation energy of this reaction.

The constant $A = 2.57 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3$.

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

[2 marks]

$$\ln k = \ln A - E_a/RT \quad \text{so} \quad E_a = RT(\ln A - \ln k)$$

$$\ln A = \ln(2.57 \times 10^{10}) = 23.97; \quad \ln k = \ln(6.51 \times 10^{-3}) = -5.03$$

$$E_a = 8.31 \times 300 \times (23.97 - (-5.03)) = 72\,300 \text{ J mol}^{-1}$$

$$E_a = 72\,300 \div 1000 = 72.3 \text{ kJ mol}^{-1}$$

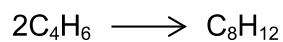
$$\text{Activation energy} = \underline{72.3 \text{ kJ mol}^{-1}}$$

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED**

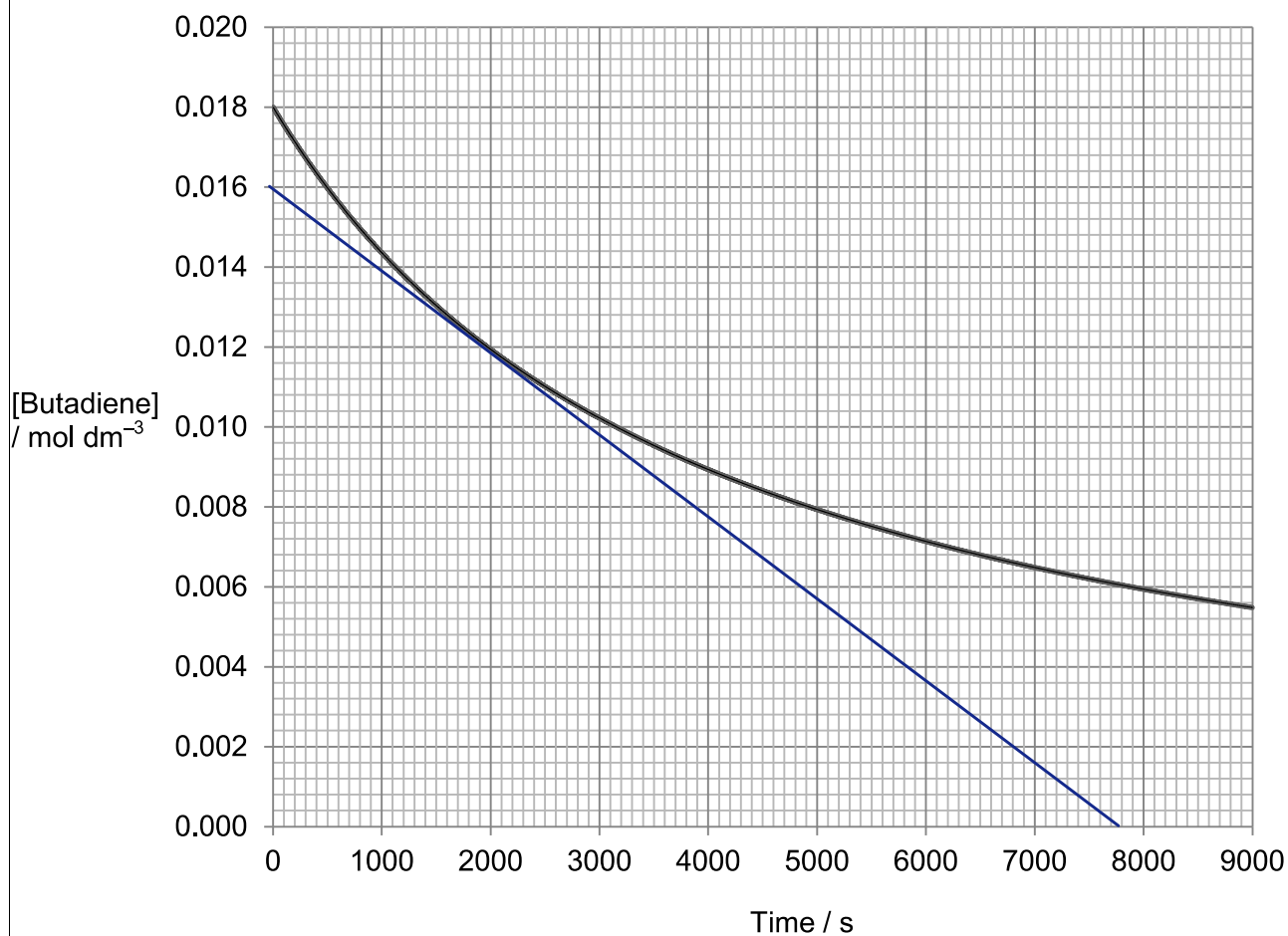
2

Butadiene dimerises according to the equation



The kinetics of the dimerisation are studied and the graph of the concentration of a sample of butadiene is plotted against time. The graph is shown in **Figure 1**.

Figure 1



0 2 . 1 Draw a tangent to the curve when the concentration of butadiene is $0.0120 \text{ mol dm}^{-3}$.

[1 mark]

0 2 . 2 The initial rate of reaction in this experiment has the value $4.57 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Use this value, together with a rate obtained from your tangent, to justify that the order of the reaction is 2 with respect to butadiene.

[5 marks]

Tangent: change in [butadiene] = -0.0160, change in time = 7800

s, so gradient = $-(0.0160 - 0) \div (7800 - 0) = -2.05 \times 10^{-6}$, so

rate at 0.0120 = $2.05 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

Initial rate $\div$ rate at 0.0120 = $(4.57 \times 10^{-6}) \div (2.05 \times 10^{-6}) =$

2.23

Initial concentration $\div$ concentration where tangent drawn = $0.018 \div$

0.012 = 1.5

If the order is 2, the rate should increase by a factor of $(1.5)^2 =$

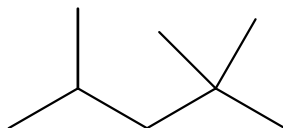
2.25. This is approximately equal to 2.23, therefore the reaction is

2nd order with respect to butadiene.

Turn over for the next question

- 3 Isooctane (C_8H_{18}) is the common name for the branched-chain hydrocarbon that burns smoothly in car engines. The skeletal formula of isooctane is shown in **Figure 2**.

Figure 2



- 0 3** . **1** Give the IUPAC name for isooctane.

[1 mark]

2,2,4-trimethylpentane

- 0 3** . **2** Deduce the number of peaks in the ^{13}C NMR spectrum of isooctane.

[1 mark]

Only **one** answer is allowed.

Completely fill in the circle alongside the appropriate answer.

CORRECT METHOD



WRONG METHODS



If you want to change your answer you must cross out your original answer as shown.

If you wish to return to an answer previously crossed out, ring the answer you now wish to select as shown.

5



6



7



8



- 0 3 . 3** Isooctane can be formed, together with propene and ethene, in a reaction in which one molecule of an alkane that contains 20 carbon atoms is cracked.

Using molecular formulas, write an equation for this reaction.

[1 mark]



- 0 3 . 4** How do the products of the reaction in Question 3.3 show that the reaction is an example of thermal cracking?

[1 mark]

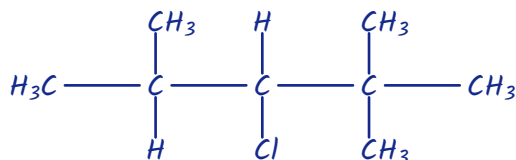
Mainly alkenes are formed (propene and ethene).

- 0 3 . 5** Deduce the number of monochloro isomers formed by isooctane. Draw the structure of the monochloro isomer that exists as a pair of optical isomers.

[2 marks]

Number of monochloro isomers 4

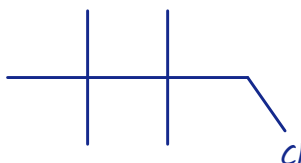
Structure



- 0 3 . 6** An isomer of isooctane reacts with chlorine to form only one monochloro compound.

Draw the **skeletal formula** of this monochloro compound.

[1 mark]



Question 3 continues on the next page

- 0 3 . 7** A sample of a monochlorooctane is obtained from a comet. The chlorine in the monochlorooctane contains the isotopes ^{35}Cl and ^{37}Cl in the ratio 1.5 : 1.0. Calculate the M_r of this monochlorooctane.

[2 marks]

$$C_8H_{17}^{35}Cl = 96.0 + 17.0 + 35.0 = 148.0$$

$$C_8H_{17}^{37}Cl = 96.0 + 17.0 + 37.0 = 150.0$$

$$M_r = (1.5 \times 148.0 + 1.0 \times 150.0) \div 2.5 = 148.8$$

$$M_r = \underline{148.8}$$

- 0 3 . 8** Isooctane reacts with an excess of chlorine to form a mixture of chlorinated compounds. One of these compounds contains 24.6% carbon and 2.56% hydrogen by mass. Calculate the molecular formula of this compound.

[3 marks]

$$\% Cl = 100 - 24.6 - 2.56 = 72.8\%$$

$$C : H : Cl = 24.6/12 : 2.56/1 : 72.8/35.5 = 2.05 : 2.56 : 2.05$$

$$\div 2.05: 1 : 1.25 : 1$$

$$\text{Whole number ratio } (\times 4) = 4 : 5 : 4, \text{ empirical formula } C_4H_5Cl_4$$

$$\text{Isooctane has 8 carbons, so MF} = 2 \times C_4H_5Cl_4$$

$$\text{Molecular formula} = \underline{C_8H_{10}Cl_8}$$

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED**

- 4 Alcohol **A** $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$ undergoes reactions separately with acidified potassium dichromate(VI) and with concentrated sulfuric acid.

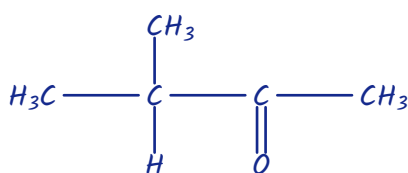
0 4 . 1 Deduce the IUPAC name for alcohol **A**.

[1 mark]

3-methylbutan-2-ol

0 4 . 2 Draw the structure of the organic product, **B**, formed when **A** is oxidised in the reaction with acidified potassium dichromate(VI).

[1 mark]



0 4 . 3 Two isomeric alkenes, **C** and **D**, are formed when **A** is dehydrated in the reaction with concentrated sulfuric acid.

Name the mechanism for this dehydration reaction.

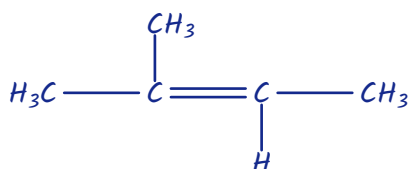
[1 mark]

Elimination

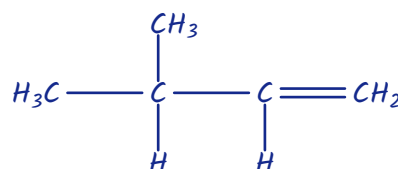
0 4 . 4 Draw the structure of each isomer.

[2 marks]

Isomer **C**



Isomer **D**



0 4 . **5** Name the type of structural isomerism shown by **C** and **D**.

[1 mark]

Position isomerism

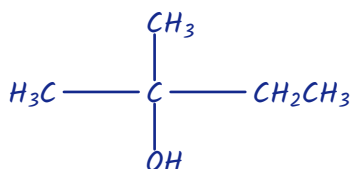
0 4 . **6** List alcohol **A**, product **B** and isomer **C** in order of increasing boiling point.

[1 mark]

C, B, A (lowest boiling point first: C < B < A)

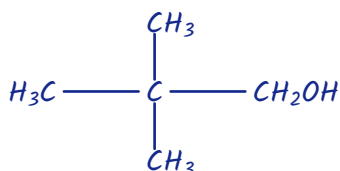
0 4 . **7** Draw the structure of the isomer of **A** that is **not** oxidised by acidified potassium dichromate(VI).

[1 mark]



0 4 . **8** Draw the structure of the isomer of **A** that **cannot** be dehydrated to form an alkene by reaction with concentrated sulfuric acid.

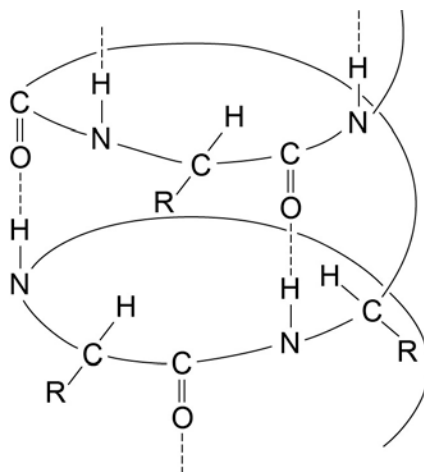
[1 mark]



Turn over for the next question

- 5 **Figure 3** shows a simplified representation of the arrangement of some amino acids in a portion of a protein structure in the form of an α -helix.

Figure 3



- 0 5 . 1 Name the type of protein structure in **Figure 3**.

[1 mark]

Secondary structure

- 0 5 . 2 Explain the origin of the interaction represented by the dotted lines in **Figure 3**.

[4 marks]

Nitrogen and oxygen are very electronegative atoms (much more electronegative than carbon and hydrogen).

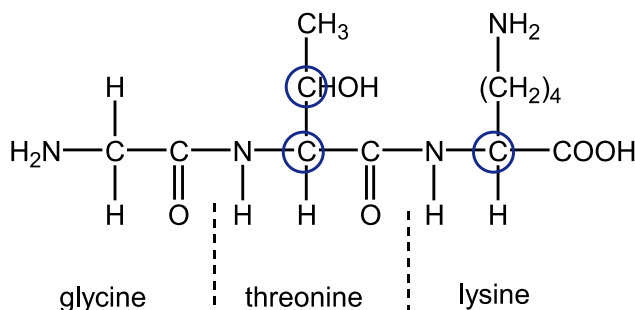
Therefore the C=O and N-H bonds are polar: the O is δ^- and the H on the N is δ^+ .

This results in the formation of a hydrogen bond between the O of a C=O group and the H of an N-H group further along the chain.

In the hydrogen bond, a lone pair of electrons on the oxygen atom is strongly attracted to the δ^+ H atom.

- 6 The tripeptide shown in **Figure 4** is formed from the amino acids glycine, threonine and lysine.

Figure 4

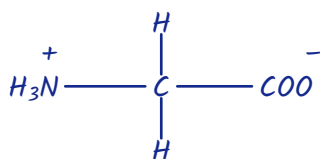


- 0 6** . **1** Draw a separate circle around **each** of the asymmetric carbon atoms in the tripeptide in **Figure 4**.

[1 mark]

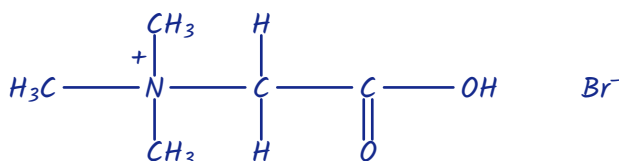
- 0 6** . **2** Draw the zwitterion of glycine.

[1 mark]



- 0 6** . **3** Draw the structure of the species formed when glycine reacts with an excess of bromomethane.

[1 mark]



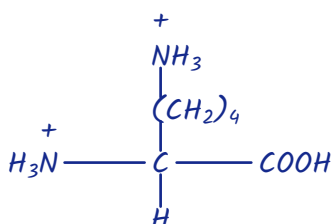
- 0 6** . **4** Deduce the IUPAC name of threonine.

[1 mark]

2-amino-3-hydroxybutanoic acid

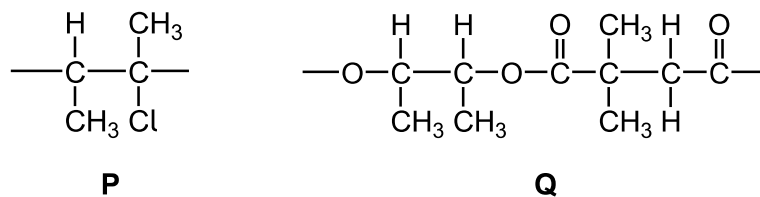
- 0 6** . **5** Draw the structure of the species formed by lysine at low pH.

[1 mark]



7 Repeating units of two polymers, **P** and **Q**, are shown in **Figure 5**.

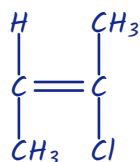
Figure 5



- 0 7 . 1** Draw the structure of the monomer used to form polymer **P**.
Name the type of polymerisation involved.

[2 marks]

Monomer

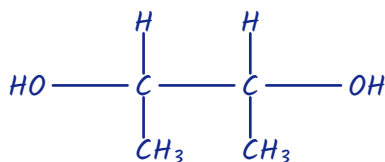


Type of polymerisation Addition

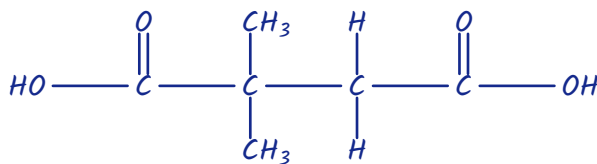
- 0 7 . 2** Draw the structures of **two** compounds that react together to form polymer **Q**.

[2 marks]

Structure of compound 1



Structure of compound 2



- 07** . **3** Suggest an environmental advantage of polymer **Q** over polymer **P**.
Justify your answer.

[3 marks]

Advantage *Q is biodegradable.*

Justification *Q contains polar C=O groups, so it has a $\delta+$ C atom*
(but P does not have a C=O group).

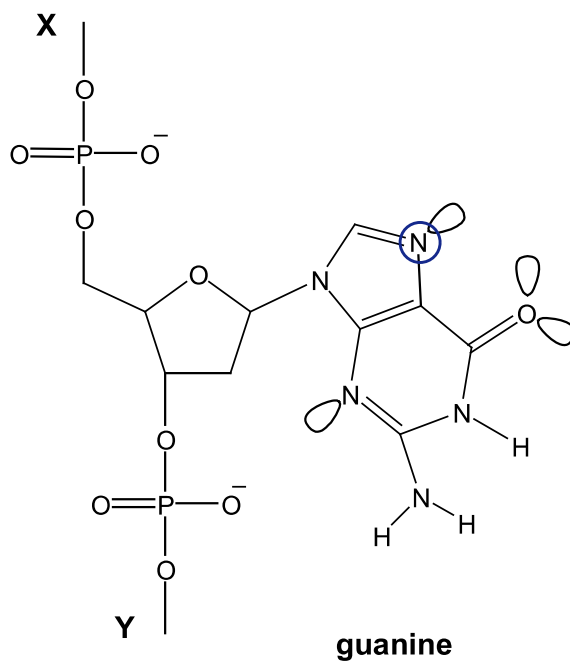
Therefore Q can be attacked by nucleophiles (e.g. water or OH^-
hydrolysing the ester links), leading to breakdown of the polymer
chain.

Turn over for the next question

8 The anticancer drug cisplatin operates by reacting with the guanine in DNA.

Figure 6 shows a small part of a single strand of DNA. Some lone pairs are shown.

Figure 6



0 8 . **1** The DNA chain continues with bonds at **X** and **Y**.

State the name of the sugar molecule that is attached to the bond at **X**.

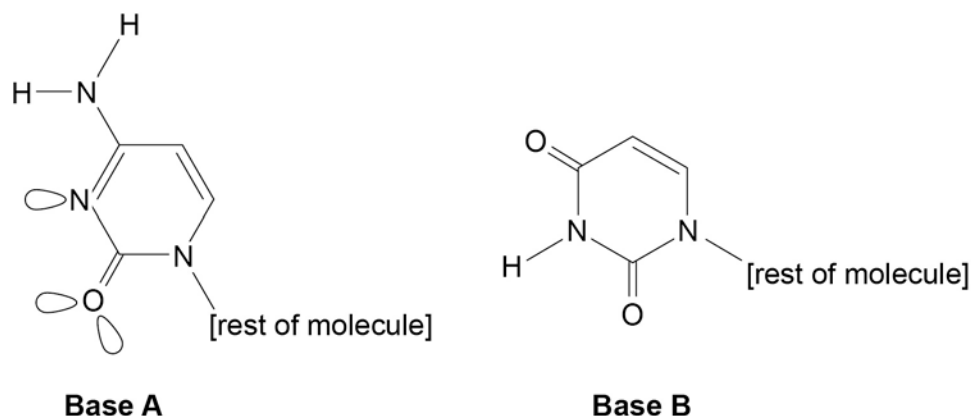
[1 mark]

2-deoxyribose

- 0 8 . 2** Messenger RNA is synthesised in cells in order to transfer information from DNA. The bases in one strand of DNA pair up with the bases used to synthesise RNA.

Figure 7 shows two bases used in RNA.

Figure 7



Suggest which of the bases **A** and **B** forms a pair with guanine in **Figure 6** when messenger RNA is synthesised.

Explain how the base that you have chosen forms a base pair with guanine.

[4 marks]

Base A (cytosine) forms a pair with guanine.

The top N-H of base A (on its NH₂ group) forms a hydrogen bond to a lone pair on the O of guanine.

The lone pair of electrons on the ring N of base A forms a hydrogen bond to the H-N (ring N-H) of guanine.

A lone pair of electrons on the O of base A forms a hydrogen bond to the lower H-N (of the NH₂) of guanine.

Question 8 continues on the next page

- 0 8** . **3** Cisplatin works because one of the atoms on guanine can form a co-ordinate bond with platinum, replacing one of the ammonia or chloride ligands. Another atom on another guanine can also form a co-ordinate bond with the same platinum by replacing another ligand.

On **Figure 6**, draw a ring round an atom in guanine that is likely to bond to platinum.

[1 mark]

- 0 8** . **4** An adverse effect of cisplatin is that it also prevents normal healthy cells from replicating.

Suggest **one** way in which cisplatin can be administered so that this side effect is minimised.

[1 mark]

*Use it in very small amounts, or target the application directly to the
tumour (e.g. inject it into the tumour).*

Turn over for the next question

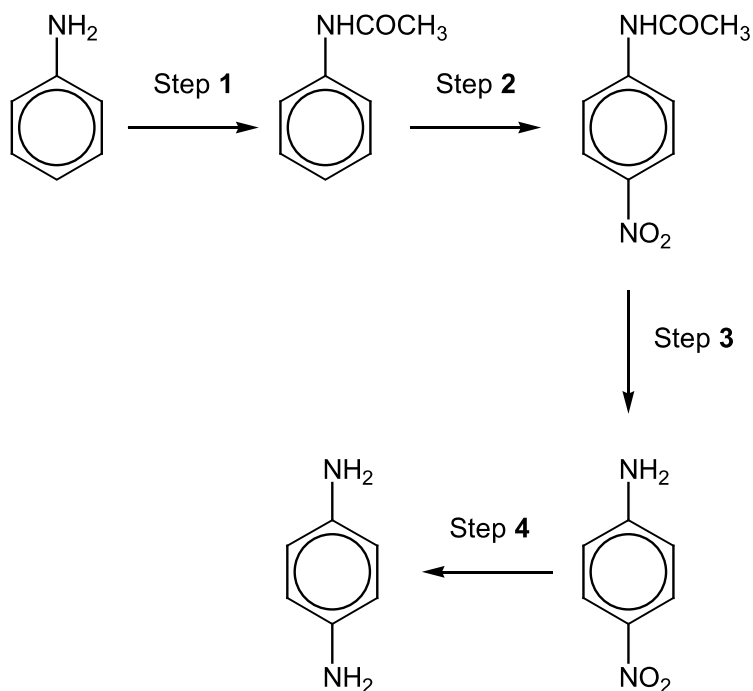
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ANSWER IN THE SPACES PROVIDED**

9

1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

A possible synthesis of 1,4-diaminobenzene from phenylamine is shown in **Figure 8**.

Figure 8



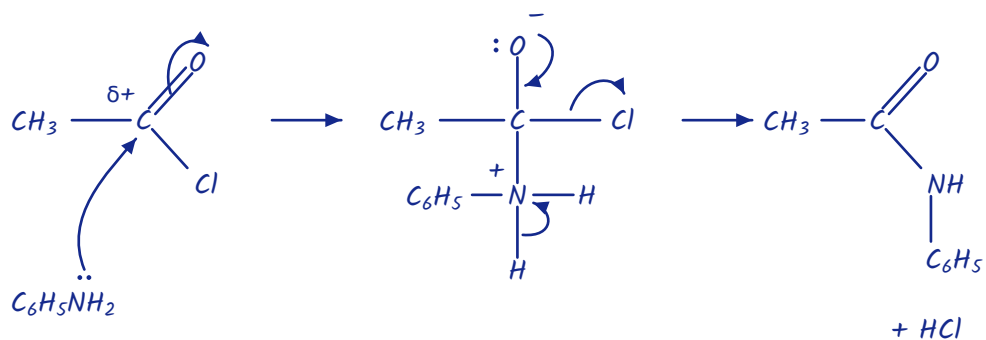
0 9 . 1 A suitable reagent for step 1 is CH_3COCl

Name and draw a mechanism for the reaction in step 1.

[5 marks]

Name of mechanism (Nucleophilic) addition-elimination

Mechanism



0 9 . 2 The product of step 1 was purified by recrystallisation as follows.

The crude product was dissolved in **the minimum quantity of hot water** and the hot solution was filtered through a hot filter funnel into a conical flask. This filtration removed any insoluble impurities. The flask was **left to cool to room temperature**.

The crystals formed were filtered off using a Buchner funnel and a clean cork was used **to compress the crystals in the funnel. A little cold water was then poured through the crystals.**

After a few minutes, the crystals were removed from the funnel and weighed. A small sample was then used to find the melting point.

Give reasons for each of the following practical steps.

[4 marks]

The minimum quantity of hot water was used

To make sure the hot solution is saturated, so that crystals form on cooling (and as little product as possible stays dissolved).

The flask was cooled to room temperature before the crystals were filtered off

The product is more soluble when warm, so the yield would be lower if the crystals were filtered off while warm.

The crystals were compressed in the funnel

So that air passes through the sample, not just round it, which dries the crystals better.

A little cold water was poured through the crystals

To wash away soluble impurities from the surface of the crystals.

Question 9 continues on the next page

0 9 . 3 The melting point of the sample in Question 9.2 was found to be slightly lower than a data-book value.

Suggest the most likely impurity to have caused this low value and an improvement to the method so that a more accurate value for the melting point would be obtained.

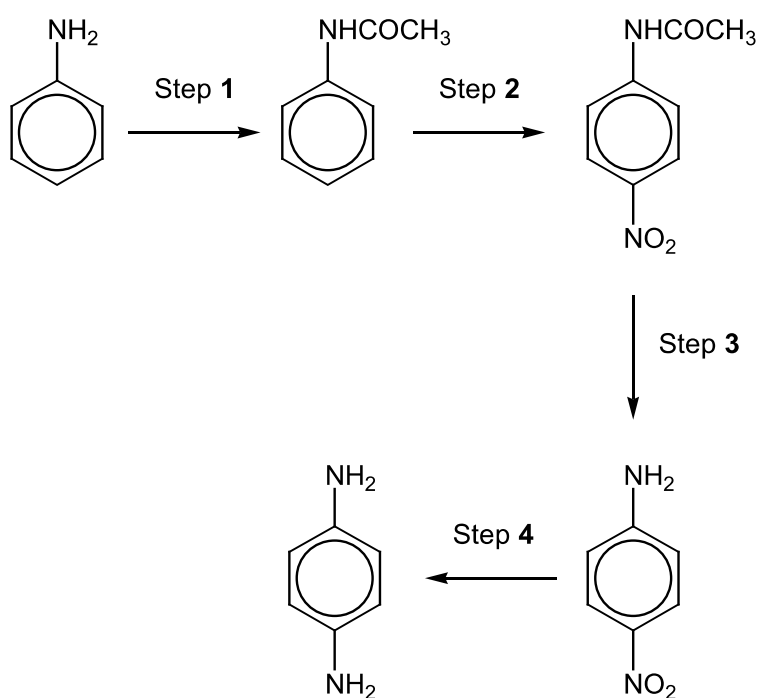
[2 marks]

The most likely impurity is water (the crystals were only in the funnel for a few minutes, so they were still wet).

Improvement: press the sample of crystals between filter papers (or leave it to dry in air) before measuring the melting point.

Figure 8 is repeated here to help you answer the following questions.

Figure 8



- 0 9 . 4 In an experiment starting with 5.05 g of phenylamine, 4.82 g of purified product were obtained in step 1.

Calculate the percentage yield in this reaction.
Give your answer to the appropriate number of significant figures.

[3 marks]



$$1 : 1 \text{ ratio, moles} = 5.05 \div 93.0 = 0.0543 \text{ mol}$$

$$\text{Expected mass} = 5.05 \times 135.0 \div 93.0 = 7.33 \text{ g}$$

$$\% \text{ yield} = (4.82 \div 7.33) \times 100 = 65.75 = 65.8\%$$

Percentage yield = 65.8 %

- 0 9 . 5 A reagent for step 2 is a mixture of concentrated nitric acid and concentrated sulfuric acid, which react together to form a reactive intermediate.

Write an equation for the reaction of this intermediate in step 2.

[1 mark]



- 0 9 . 6 Name a mechanism for the reaction in step 2.

[1 mark]

Electrophilic substitution

- 0 9 . 7 Suggest the type of reaction occurring in step 3.

[1 mark]

Hydrolysis (of the amide)

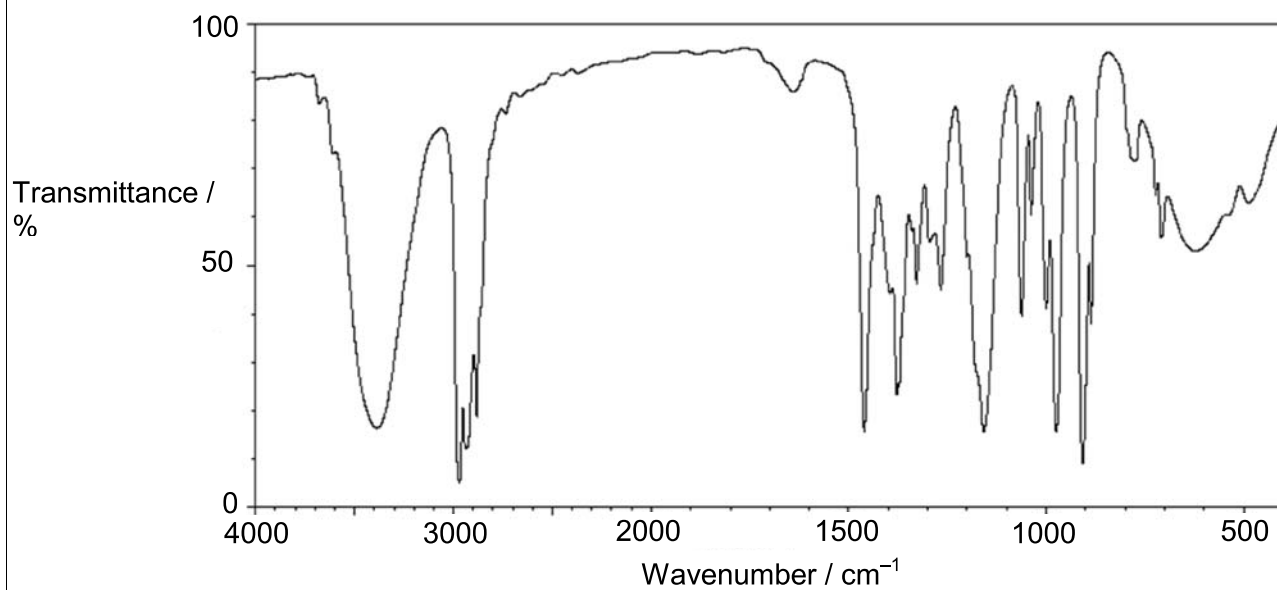
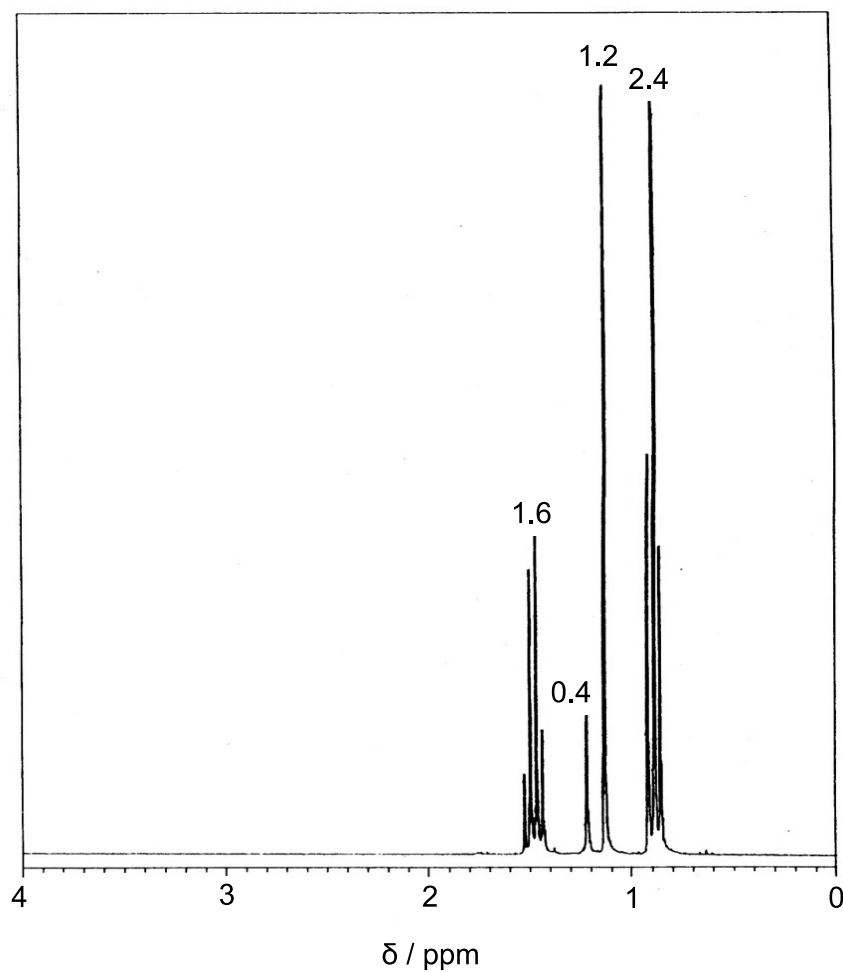
- 0 9 . 8 Identify the reagents used in step 4.

[1 mark]

Tin and hydrochloric acid (Sn / HCl)

10

The infrared spectrum (**Figure 9**) and the ^1H NMR spectrum (**Figure 10**) of compound **R** with molecular formula $\text{C}_6\text{H}_{14}\text{O}$ are shown.

Figure 9**Figure 10**

1 0

The relative integration values for the NMR peaks are shown on **Figure 10**.

Deduce the structure of compound **R** by analysing **Figure 9** and **Figure 10**. Explain each stage in your deductions.

Use **Table A** and **Table B** on the Data Sheet.

[8 marks]

IR: the broad absorption at about 3360 cm^{-1} shows an O-H group, so R is an alcohol (there is no C=O absorption at 1680 to 1750 cm^{-1}).

NMR: there are 4 peaks, which indicates 4 different environments of hydrogen.

The integration ratio is 1.6 : 0.4 : 1.2 : 2.4, so the simplest whole number ratio is 4 : 1 : 3 : 6 (14 H in total, as in $\text{C}_6\text{H}_{14}\text{O}$).

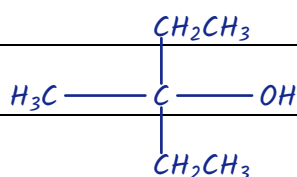
The singlet with integration 1 ($\delta = 1.2\text{ ppm}$) must be caused by the H in the OH of the alcohol.

The singlet with integration 3 ($\delta = 1.1\text{ ppm}$) must be due to a CH_3 group with no adjacent H (it is on a carbon with no H).

The quartet ($\delta = 1.5\text{ ppm}$) and the triplet ($\delta = 0.9\text{ ppm}$) suggest a CH_2CH_3 group (CH_2 next to CH_3 gives a quartet, CH_3 next to CH_2 gives a triplet).

Integration 4 for the quartet and 6 for the triplet indicates two equivalent CH_2CH_3 groups.

So a central C with no H is bonded to OH, CH_3 and two CH_2CH_3 groups: R is 3-methylpentan-3-ol, $\text{CH}_3\text{C}(\text{OH})(\text{CH}_2\text{CH}_3)_2$.



Turn over for the next question

- 11 Butanone is reduced in a two-step reaction using NaBH_4 followed by dilute hydrochloric acid.

1

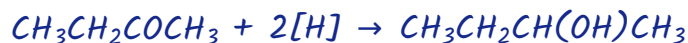
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1

 Write an overall equation for the reduction of butanone using $[\text{H}]$ to represent the reductant.

[1 mark]



1

1

 .

2

 By considering the mechanism of the reaction, explain why the product has **no** effect on plane polarised light.

[6 marks]

Stage 1: The mechanism is nucleophilic addition. The hydride ion (H^-) from NaBH_4 acts as a nucleophile and attacks the δ^+ carbon of the $\text{C}=\text{O}$ group, then the O^- formed is protonated (by H^+ from the dilute HCl) to give the alcohol.

The carbonyl group in butanone is planar (trigonal planar around the $\text{C}=\text{O}$ carbon), so the H^- can attack from either side of the plane (above or below) with equal probability.

Stage 2: The product is butan-2-ol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$. Carbon 2 has four different groups (H , OH , CH_3 and C_2H_5), so it is chiral and the product exists in two chiral forms (enantiomers).

Attack from one side gives one enantiomer and attack from the other side gives the other, so equal amounts of each enantiomer are formed: a racemic mixture.

Stage 3: Each enantiomer rotates the plane of polarised light by the same amount but in opposite directions. In the racemic mixture the effects cancel, so the product has no effect on plane polarised light.

12 But-1-ene reacts with a reagent of the form HY to form a saturated compound.

1 2 . 1 Suggest a reagent of the form HY which reacts with but-1-ene.

[1 mark]

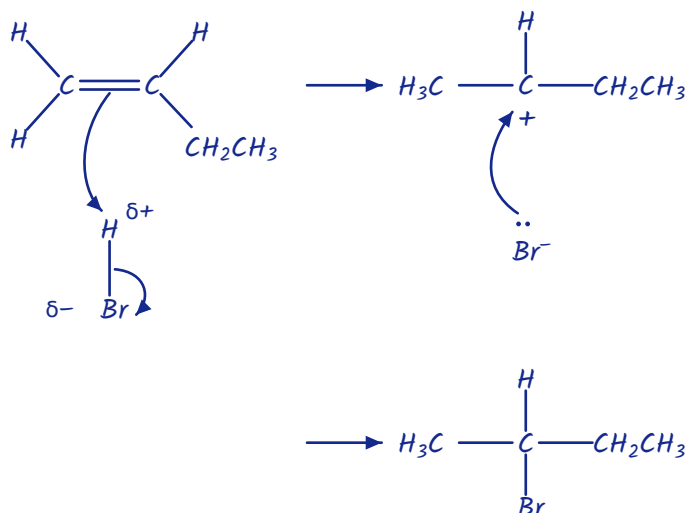
HBr (hydrogen bromide)

1 2 . 2 Name and draw a mechanism for the reaction in Question 12.1.

[5 marks]

Name of mechanism *Electrophilic addition*

Mechanism



1 2 . 3 Explain how three isomeric products are formed when HY reacts with but-1-ene.

[3 marks]

The major product, 2-bromobutane, is formed via the more stable secondary carbocation. It has a chiral carbon and the planar carbocation can be attacked by Br⁻ from either side, so the major product exists as a pair of enantiomers (two isomers).

The third isomer is 1-bromobutane, the minor product, because it is obtained via the less stable primary carbocation.

END OF QUESTIONS

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