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Candidate surname

Other names

Pearson Edexcel
International
Advanced Level

Centre Number

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Tuesday 11 June 2019

Afternoon (Time: 1 hour 40 minutes)

Paper Reference **WCH05/01**

Chemistry

Advanced

**Unit 5: General Principles of Chemistry II – Transition Metals
and Organic Nitrogen Chemistry
(including synoptic assessment)**

**Candidates must have: Scientific calculator
Data Booklet**

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
– *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.

Turn over ►

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SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box . If you change your mind, put a line through the box and then mark your new answer with a cross .

1 In which of these ions does the metal have an oxidation number of +2?

- A AlO_2^-
- B $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$
- C $[\text{Fe}(\text{CN})_6]^{4-}$
- D VO^{2+}

(Total for Question 1 = 1 mark)

2 Iodine is manufactured by the reduction of iodate(V) ions, IO_3^- , using hydrogensulfite ions, HSO_3^- . In this reaction, the hydrogensulfite ions are oxidised to sulfate ions, SO_4^{2-} .

By considering the relevant oxidation numbers, the number of moles of hydrogensulfite ions needed to reduce 1 mol of iodate(V) ions is

- A 0.4
- B 1
- C 2.5
- D 5

(Total for Question 2 = 1 mark)

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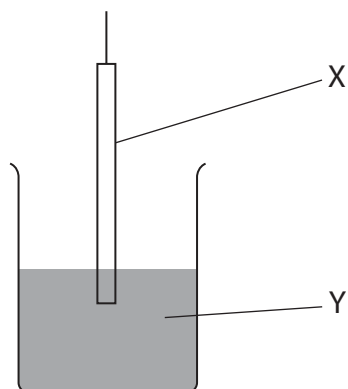
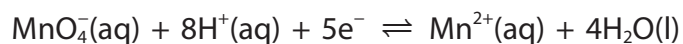
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3 An electrode system and a diagram of its half-cell are shown.



(a) Identify the oxidising agent and X in the half-cell.

(1)

	Oxidising agent	X
<input type="checkbox"/> A	MnO_4^-	platinum
<input type="checkbox"/> B	MnO_4^-	manganese
<input type="checkbox"/> C	Mn^{2+}	platinum
<input type="checkbox"/> D	Mn^{2+}	manganese

(b) As well as water, which components must be present in Y?

(1)

- A $\text{Mn}^{2+}(\text{aq})$ and $\text{H}^+(\text{aq})$ only
- B $\text{MnO}_4^-(\text{aq})$ and $\text{H}^+(\text{aq})$ only
- C $\text{MnO}_4^-(\text{aq})$ and $\text{Mn}^{2+}(\text{aq})$ only
- D $\text{MnO}_4^-(\text{aq})$, $\text{Mn}^{2+}(\text{aq})$ and $\text{H}^+(\text{aq})$ only

(Total for Question 3 = 2 marks)



- 4 For any reaction, $E_{\text{cell}}^{\ominus}$ is related to the entropy change and also to the equilibrium constant, K , for that reaction.

$E_{\text{cell}}^{\ominus}$ is directly proportional to both

- A ΔS_{system} and K .
- B ΔS_{system} and $\ln K$.
- C ΔS_{total} and K .
- D ΔS_{total} and $\ln K$.

(Total for Question 4 = 1 mark)

- 5 In the ethanol-oxygen fuel cell, the ethanol is

- A oxidised at the anode.
- B oxidised at the cathode.
- C reduced at the anode.
- D reduced at the cathode.

(Total for Question 5 = 1 mark)

- 6 Which element could form a colourless ion with an oxidation number of +4?

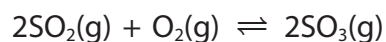
- A Titanium
- B Manganese
- C Iron
- D Copper

(Total for Question 6 = 1 mark)

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- 7 The conversion of sulfur dioxide to sulfur trioxide is catalysed by vanadium(V) oxide.



The mechanism of this reaction is most likely to involve the

- A reduction of vanadium(V) to vanadium(IV) by oxygen followed by the oxidation of vanadium(IV) to vanadium(V) by sulfur dioxide.
- B reduction of vanadium(V) to vanadium(IV) by sulfur dioxide followed by the oxidation of vanadium(IV) to vanadium(V) by oxygen.
- C oxidation of vanadium(V) to vanadium(VI) by oxygen followed by the reduction of vanadium(VI) to vanadium(V) by sulfur dioxide.
- D oxidation of vanadium(V) to vanadium(VI) by sulfur dioxide followed by the reduction of vanadium(VI) to vanadium(V) by oxygen.

(Total for Question 7 = 1 mark)

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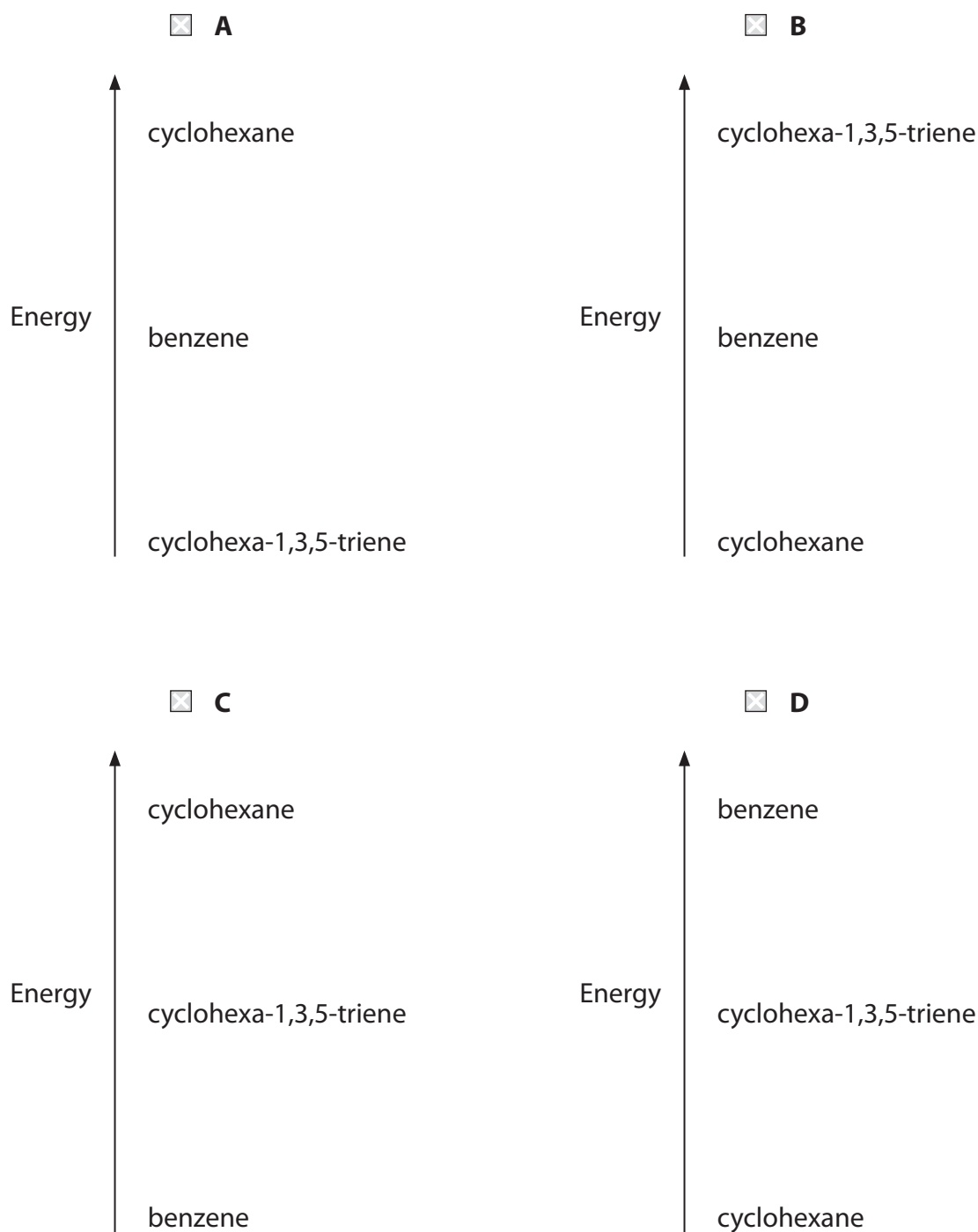
- 8 Benzene has a delocalised electronic structure that makes it 150 kJ mol^{-1} more stable than the structure with alternate single and double bonds, which would be called cyclohexa-1,3,5-triene.

The hydrogenation of benzene to cyclohexane has an enthalpy change

$$\Delta H_{\text{reaction}}^{\ominus} = -205 \text{ kJ mol}^{-1}$$

Which energy level diagram represents these energy differences?

The diagrams are not to scale.



(Total for Question 8 = 1 mark)



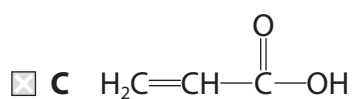
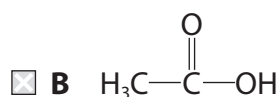
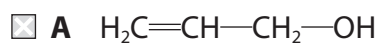
9 An organic compound **R** has the following reactions:

R reacts with sodium hydroxide to form an ionic compound

R decolourises bromine water

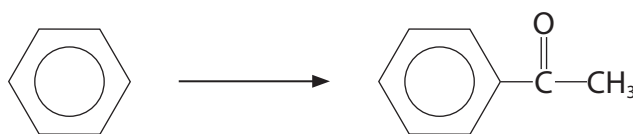
R reacts with ethanol, in the presence of an acid catalyst, to form a sweet-smelling product.

Compound **R** could be



(Total for Question 9 = 1 mark)

10 Benzene reacts under suitable conditions with a compound **S** to form phenylethanone.



Compound **S** is

- A** ethanal.
 B ethanoic acid.
 C ethanoyl chloride.
 D propanone.

(Total for Question 10 = 1 mark)

11 These four compounds can be used in the preparation of polymers.

E	$\text{CH}_3\text{---CH}_2\text{---}\overset{\text{CH}_3}{\text{C}}\text{=CH}_2$
F	$\text{Cl---}\overset{\text{O}}{\parallel}{\text{C}}\text{---CH}_2\text{---CH}_2\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---Cl}$
G	$\text{H}_2\text{N---CH}_2\text{---}\text{C}_6\text{H}_4\text{---CH}_2\text{---NH}_2$
H	$\text{HO---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---OH}$

Which monomer or combination of monomers would **not** produce a polymer?

- A E
- B F
- C F reacting with G
- D F reacting with H

(Total for Question 11 = 1 mark)

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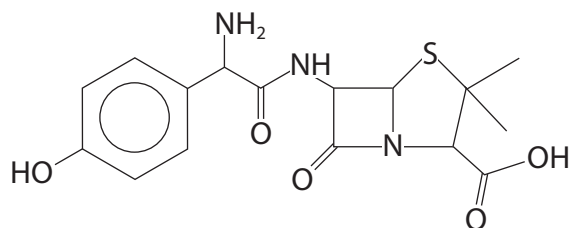


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12 Amoxicillin is an antibiotic.



(a) Which of the following functional groups is **not** present in the structure of amoxicillin? (1)

- A Amine
- B Amide
- C Ketone
- D Phenol

(b) Which of these is the most likely structure of amoxicillin at pH = 5? (1)

- A

Structure A shows amoxicillin with the amino group on the side chain protonated to an ammonium group (NH_3^+). The phenol group is neutral (OH).
- B

Structure B shows amoxicillin with the amino group on the side chain neutral (NH_2) and the phenol group protonated to a phenolium ion ($^+\text{H}_2\text{O}$).
- C

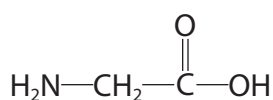
Structure C shows amoxicillin with the amino group on the side chain neutral (NH_2) and the phenol group deprotonated to a phenoxide ion (^-O).
- D

Structure D shows amoxicillin with the amino group on the side chain neutral (NH_2) and the carboxyl group protonated to a carboxonium ion (OH_2^+).

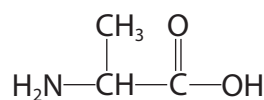
(Total for Question 12 = 2 marks)



13 Glycine and alanine are the two simplest amino acids.



glycine



alanine

(a) Amino acids are crystalline solids at room temperature.

When the solids melt, the main forces broken are

(1)

- A covalent bonds.
- B hydrogen bonds.
- C ionic bonds.
- D London forces.

(b) Which of these amino acids could rotate the plane of plane-polarised light?

(1)

- A Both glycine and alanine
- B Neither glycine nor alanine
- C Only glycine
- D Only alanine

(c) Glycine and alanine combine to form two possible dipeptides.

What are the structures of these dipeptides?

(1)

- A $\text{H}_2\text{NCH}_2\text{COONHCH}(\text{CH}_3)\text{COOH}$ and $\text{H}_2\text{NCH}(\text{CH}_3)\text{COONHCH}_2\text{COOH}$
- B $\text{H}_2\text{NCH}_2\text{CONHCH}(\text{CH}_3)\text{COOH}$ and $\text{H}_2\text{NCH}(\text{CH}_3)\text{COONHCH}_2\text{COOH}$
- C $\text{H}_2\text{NCH}_2\text{COONHCH}(\text{CH}_3)\text{COOH}$ and $\text{H}_2\text{NCH}(\text{CH}_3)\text{CONHCH}_2\text{COOH}$
- D $\text{H}_2\text{NCH}_2\text{CONHCH}(\text{CH}_3)\text{COOH}$ and $\text{H}_2\text{NCH}(\text{CH}_3)\text{CONHCH}_2\text{COOH}$

(Total for Question 13 = 3 marks)



14 Propanenitrile ($\text{CH}_3\text{CH}_2\text{CN}$) may be converted into propanoic acid by reaction with aqueous sodium hydroxide followed by dilute sulfuric acid.

The purpose of the sulfuric acid is to

- A catalyse the reaction.
- B protonate the propanoate ion.
- C hydrolyse the nitrile.
- D neutralise the sodium hydroxide.

(Total for Question 14 = 1 mark)

15 In the high resolution proton nmr spectrum of propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, there are

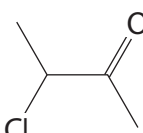
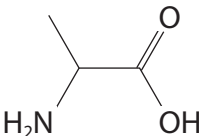
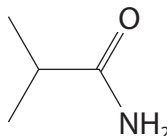
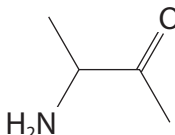
- A one singlet, two triplets and one sextet.
- B one singlet, two doublets and one triplet.
- C one singlet, two triplets and one quartet.
- D three triplets and one quartet.

(Total for Question 15 = 1 mark)

16 An organic compound forms a pale yellow precipitate when warmed with iodine and sodium hydroxide.

It also forms a soluble white solid with dilute sulfuric acid.

The structure of the compound could be

- A 
- B 
- C 
- D 

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS



SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

17 This question is about chromium and its compounds. Some data are given in the table.

Electrode reaction	E^\ominus / V
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33

(a) One of the most important uses of chromium is in plating other metals such as steel and brass. This gives them a hard shiny coating which is very resistant to corrosion.

(i) Calculate E_{cell}^\ominus for the reaction of chromium with oxygen in the presence of water.

Write the equation for this reaction. State symbols are not required.

(3)

(ii) By considering the E_{cell}^\ominus value calculated in (a)(i), suggest why a chromium coating is corrosion resistant.

(2)

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(b) The common oxidation states of chromium are +2, +3 and +6.
Chromium(III) compounds are the most stable.

- (i) Select a reagent from the table that could be used to convert chromium(III) to chromium(II) in aqueous solution.

Justify your answer by calculating the relevant $E_{\text{cell}}^{\ominus}$ value.

(2)

- (ii) When chromium(III) is converted to chromium(II) in aqueous solution, air has to be kept out of the apparatus.

Explain why this is necessary.

(2)

- (iii) State the colour **change** that you would see when chromium(III) is converted to chromium(II) in aqueous solution.

(1)



*(iv) Explain why solutions of chromium(II) and chromium(III) have **different** colours.

(3)

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(c) Chromium(III) forms a very large number of complexes.

(i) Give the formula and name the shape of the resulting complex when excess hydrochloric acid is added to a solution of chromium(III) ions.

(1)

Formula

Shape

(ii) Give the formula and name the shape of the resulting complex when excess ammonia is added to a solution of chromium(III) ions.

(1)

Formula

Shape



(d) The most common ions in which chromium has the oxidation number +6 are chromate(VI) and dichromate(VI).

(i) Write an equation showing the conversion of chromate(VI) ions into dichromate(VI) ions. State symbols are not required.

(2)

*(ii) Suggest why the $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}(\text{aq})$ ion does **not** exist.

(3)

(iii) If the $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}$ ion **did** exist, suggest what colour the solution would be. Justify your answer.

(1)



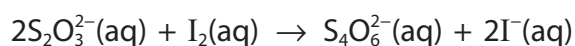
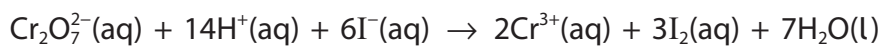
- (e) Potassium dichromate(VI) crystals are very stable so the compound is used to determine the exact concentration of sodium thiosulfate solutions.

Excess potassium iodide and dilute sulfuric acid were added to 10.00 cm³ of a potassium dichromate(VI) solution of concentration 0.0495 mol dm⁻³.

The resulting solution was titrated with sodium thiosulfate solution.

The mean titre was 19.50 cm³.

The equations for the reactions are



- (i) Identify the indicator that would be used in this titration and give the colour change at the end-point.

(2)

- (ii) Calculate the concentration of the sodium thiosulfate solution.

(4)

(Total for Question 17 = 27 marks)

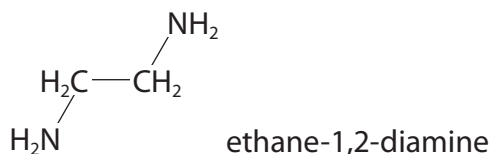


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18 Ethane-1,2-diamine (also called ethylenediamine) is a colourless liquid with a smell similar to ammonia. Ethane-1,2-diamine is used in the production of pharmaceuticals, polymers and agricultural chemicals.



(a) Outline a laboratory synthesis of ethane-1,2-diamine from ethene.

Identify reagents, essential conditions and any intermediate compounds.

(4)

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(b) When nitric acid was added to ethane-1,2-diamine and the resulting solution allowed to evaporate to dryness at room temperature, white crystals remained. Explain the chemical reaction that occurred and give the structure of the white crystals.

(3)

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(c) Ethane-1,2-diamine forms a complex with copper(II) ions.

(i) Draw a diagram of a complex that copper(II) ions form with ethane-1,2-diamine. (1)

*(ii) When ethane-1,2-diamine is added to an aqueous solution of tetraamminecopper(II) ions, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the formation of the ethane-1,2-diamine complex is favoured. Explain why this is so. (2)

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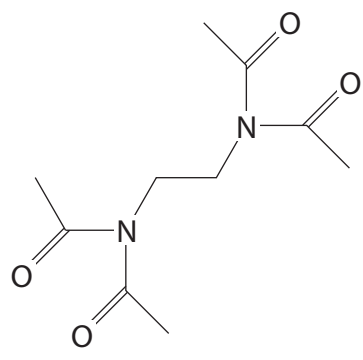


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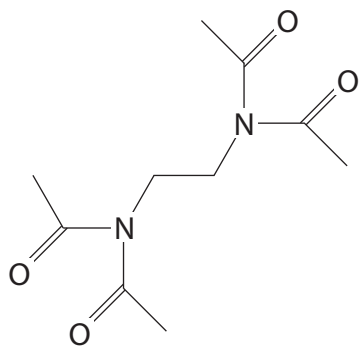
(d) Tetraacetythylenediamine (TAED) is an important component of laundry detergents that use 'active oxygen' bleaching agents. TAED is manufactured from ethane-1,2-diamine.



tetraacetythylenediamine

(i) Identify a reagent that could be used to convert ethane-1,2-diamine into TAED. (1)

(ii) State the number of peaks and relative peak areas present in the **low** resolution proton nmr spectrum of TAED. Justify your answer by referring to the diagram of the compound. (3)



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(Total for Question 18 = 14 marks)



19 A white solid **M** has the following percentage composition by mass: carbon 72.97%; hydrogen 5.41%; oxygen 21.62%.

The mass spectrum of **M** has a molecular ion peak at $m/e = 148$.

- (a) Calculate the empirical formula of **M** and hence deduce its molecular formula.
You **must** show your working.

(4)

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(b) The mass spectrum of **M** had a significant peak at $m/e = 77$.

When **M** was added to a solution of sodium hydrogencarbonate, vigorous effervescence occurred.

M decolourised a cold dilute solution of acidified potassium manganate(VII).

(i) Use this information to identify the three functional groups present in **M**. Justify your answers.

(3)

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(ii) Draw **three** possible structures of **M**.

(3)

(Total for Question 19 = 10 marks)

TOTAL FOR SECTION B = 51 MARKS



SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

20

Organic Synthesis

Organic synthesis is the preparation of a specific compound, the 'target molecule'. In some cases the target molecule is a naturally occurring compound, such as penicillin, which needs to be manufactured on a large scale. In other cases, it may be an entirely new compound that theory indicates might have desirable properties. Some of the techniques of organic synthesis are listed.

- Ascent of the homologous series is when a carbon atom is added to a carbon chain. This often involves the use of a nitrile group, either nucleophilic substitution of halogenoalkanes by a cyanide ion or nucleophilic addition of carbonyl compounds by hydrogen cyanide.
- Descent of the homologous series is when a carbon atom is removed from a carbon chain. One method of achieving this is with the iodoform reaction.
- Sometimes a functional group needs to be moved along a carbon chain. One way of achieving this is by elimination followed by addition.
- Benzenediazonium ions are important intermediates in aromatic synthesis. Their coupling reactions form azo dyes and, unlike other groups attached directly to a benzene ring, they readily undergo nucleophilic substitution reactions.

Organic synthesis is made easier by accurate knowledge of the mechanisms of the reactions involved.

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(a) Outline a synthesis of butan-1-ol from 1-bromopropane.
Give the reagents and essential conditions for each step and identify the
intermediate compounds formed.

(5)

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(b) Outline a possible method of converting 1-bromobutane into 2-bromobutane.
Give the reagents and essential conditions for each step and identify the
intermediate compound formed.

(3)

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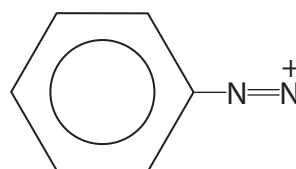
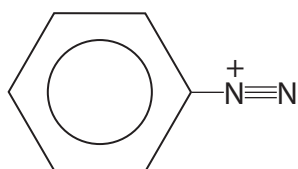
(c) The benzenediazonium ion is prepared from phenylamine (aniline).

- (i) State the reagents and conditions for the conversion of phenylamine into benzenediazonium chloride.

(2)

- (ii) Two possible structures of the benzenediazonium ion are given. Use curly arrows and relevant lone pairs to show how **each** of these structures is converted into the other.

(2)



- (iii) Benzenediazonium ions react with phenol to form an azo dye. Draw the structure of the azo dye and name the type and mechanism of the reaction occurring.

(2)

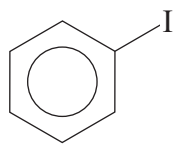


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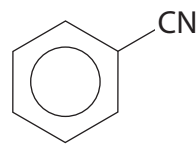
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(d) Examples of reactions in which benzenediazonium ions undergo nucleophilic substitution include the formation of iodobenzene and benzenenitrile, with nitrogen gas as the other product. These reactions are often catalysed by copper(I) ions.



iodobenzene



benzenenitrile

*(i) Suggest why the nucleophilic substitution of groups attached directly to a benzene ring is normally very difficult, and why benzenediazonium ions readily undergo nucleophilic substitution.

(2)

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(ii) State why copper(I) ions are likely to show catalytic properties.

(1)

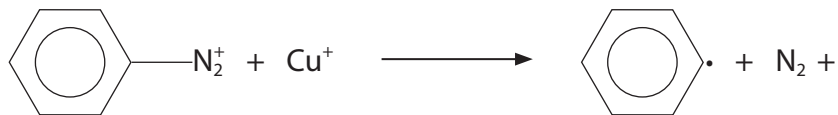
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(iii) Complete the mechanism for the nucleophilic substitution of benzenediazonium ions by iodide ions, by adding the missing species. The reaction is catalysed by copper(I) ions. Curly arrows are not required.

(2)



(Total for Question 20 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS

TOTAL FOR PAPER = 90 MARKS

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