Paper Reference(s) **WCH05/01**

**Pearson Edexcel International Advanced Level**

# Chemistry

## Advanced

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

**Monday 19 June 2017 – Morning**

**Time: 1 hour 40 minutes plus your additional time allowance**

**INSTRUCTIONS TO CANDIDATES**

**Write your centre number, candidate number, surname, other names and your signature in the boxes below. Check that you have the correct question paper.**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Centre No. | | | | | | | | |
| Candidate No. | | | | | | | | |
| Surname | | | | | | | | |
| Other names | | | | | | | | |
| Signature | | | | | | | | |
| Paper Reference | W | C | H | 0 | 5 | / | 0 | 1 |

- Use BLACK ink or BLACK ball-point pen.
- Answer ALL questions.
- Answer the questions in the spaces provided – there may be more space than you need.

**MATERIALS REQUIRED FOR EXAMINATION**
Data Booklet
Scientific calculator

**ITEMS INCLUDED WITH QUESTION PAPERS**
Periodic Table

**INFORMATION FOR CANDIDATES**
- 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 provided.

**ADVICE TO CANDIDATES**
- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

(Turn over)

## 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 Which of these elements is a transition metal?**

- ☐ **A** scandium
- ☐ **B** tin
- ☐ **C** titanium
- ☐ **D** zinc

**(TOTAL FOR QUESTION 1 = 1 MARK)**

**(Questions continue on next page)**

2 Thallium(III) ions oxidise iodide ions to iodine.

$$2I^- \longrightarrow I_2 + 2e^-$$

0·0012 mol of $Tl^{3+}$ ions oxidised 0·0024 mol iodide ions.

What is the oxidation number of the thallium ions produced in this reaction?

☐ A +1

☐ B +2

☐ C +4

☐ D +5

**(TOTAL FOR QUESTION 2 = 1 MARK)**

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(Questions continue on next page)

3 The $[Cu(H_2O)_6]^{2+}$ ion is blue because the water ligands split the 3d subshell and a 3d electron is promoted to a higher energy level

☐ A absorbing all but blue light as it drops back to its ground state.

☐ B emitting blue light as it drops back to its ground state.

☐ C absorbing all but blue light.

☐ D emitting all but blue light.

**(TOTAL FOR QUESTION 3 = 1 MARK)**

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(Questions continue on next page)

4 Ammonium vanadate(V), $NH_4VO_3$, dissolves in aqueous sodium hydroxide solution releasing a colourless gas. The gas gives a pale blue precipitate with aqueous copper(II) sulfate.

What is the colourless gas?

☐ A $H_2$

☐ B $N_2$

☐ C $NH_3$

☐ D $O_2$

**(TOTAL FOR QUESTION 4 = 1 MARK)**

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(Questions continue on next page)

5 $25{\cdot}0\,cm^3$ of a $0{\cdot}0100\,mol\,dm^{-3}$ solution of vanadium(II) ions is titrated with an acidified solution containing $0{\cdot}0200\,mol\,dm^{-3}$ manganate(VII) ions, $MnO_4^-$.

$$3MnO_4^- + 5V^{2+} + 4H^+ \longrightarrow 3Mn^{2+} + 5VO_2^+ + 2H_2O$$

What volume, in $cm^3$, of this solution of manganate(VII) ions is needed for the reaction?

☐ A 7·5

☐ B 15·0

☐ C 20·8

☐ D 41·7

**(TOTAL FOR QUESTION 5 = 1 MARK)**

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(Questions continue on next page)

6 Manganate(VII) ions, $MnO_4^-$, react with ethanedioate ions, $C_2O_4^{2-}$, in acid solution.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

What is the CHANGE in oxidation number of each carbon atom in this reaction?

☐ A +1

☐ B +3

☐ C +4

☐ D +5

**(TOTAL FOR QUESTION 6 = 1 MARK)**

(Questions continue on next page)

7 The standard electrode potential for the $Ag^+(aq)|Ag(s)$ electrode is measured.

Which is the only suitable chemical for the solution in a salt bridge to connect the silver electrode to the standard hydrogen electrode?

☐ A potassium carbonate

☐ B potassium chloride

☐ C potassium iodide

☐ D potassium nitrate

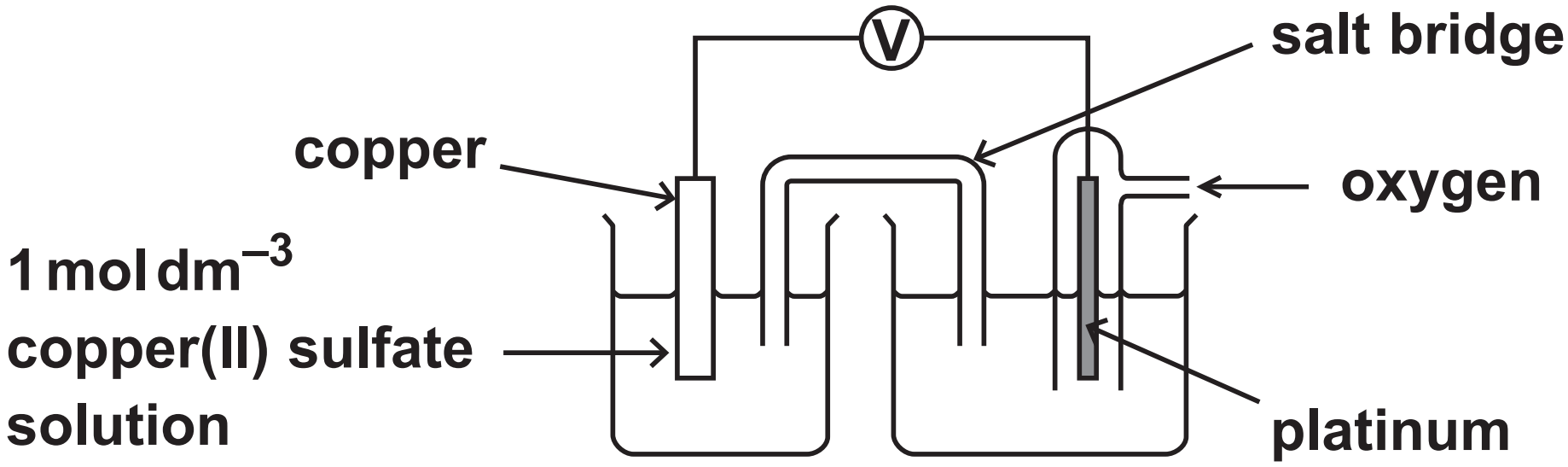
(TOTAL FOR QUESTION 7 = 1 MARK)

(Questions continue on next page)

8 The cell below was set up. Copper is the negative electrode.

The solution in the right-hand beaker contained a suitable electrolyte and phenolphthalein.

After some time, the solution in the right-hand beaker turned pink.




Which ionic half-equation shows the reaction at the oxygen electrode that caused the phenolphthalein to turn pink?

☐ A $\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

☐ B $H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

☐ C $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

☐ D $2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

**(TOTAL FOR QUESTION 8 = 1 MARK)**

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(Questions continue on next page)

9 Use these electrode potentials to answer the following questions.

| Electrode reaction | $E^{\ominus}$ / V |
|---|---|
| $Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$ | –0·41 |
| $\frac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq)$ | +0·54 |
| $\frac{1}{2}Br_2(aq) + e^- \rightleftharpoons Br^-(aq)$ | +1·09 |
| $\frac{1}{2}Cr_2O_7^{2-}(aq) + 7H^+(aq) + 3e^- \rightleftharpoons Cr^{3+}(aq) + 3\frac{1}{2}H_2O(l)$ | +1·33 |
| $\frac{1}{2}Cl_2(aq) + e^- \rightleftharpoons Cl^-(aq)$ | +1·36 |

(a) Which of these species is the strongest reducing agent? (1 mark)

☐ A $Cr^{2+}(aq)$

☐ B $Cr^{3+}(aq)$

☐ C $Cl^-(aq)$

☐ D $Cl_2(aq)$

(Question continues on next page)

(b) Which halogen(s) would oxidise chromium(II) to chromium(III) but NOT to chromium(VI) under standard conditions? (1 mark)

☐ A $Br_2(aq)$ only

☐ B $I_2(aq)$ only

☐ C $Br_2(aq)$ and $Cl_2(aq)$ only

☐ D $I_2(aq)$ and $Br_2(aq)$ only

**(TOTAL FOR QUESTION 9 = 2 MARKS)**

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10 The information about benzene NOT provided by X-ray diffraction is that

☐ A all C—C—C bond angles are the same.

☐ B all C—C bond lengths are the same.

☐ C all C—C bond energies are the same.

☐ D the molecule is planar.

**(TOTAL FOR QUESTION 10 = 1 MARK)**

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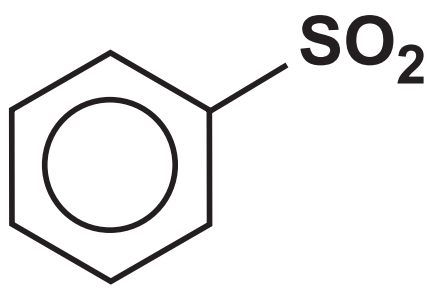
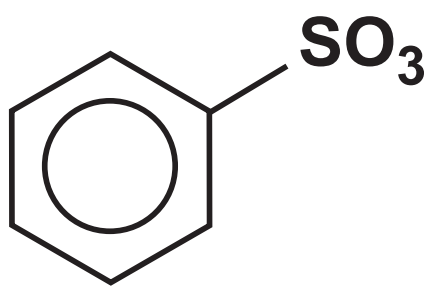
(Questions continue on next page)

**11 The formula of the organic product of the reaction between benzene and fuming sulfuric acid is**

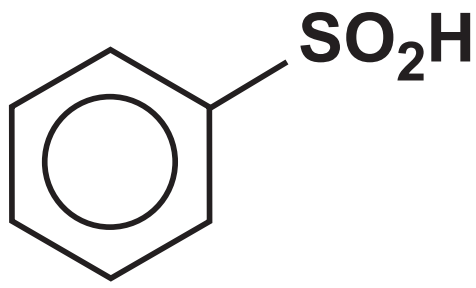
☐ **A**



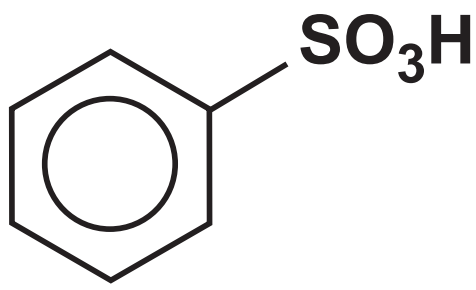

☐ **B**




☐ **C**




☐ **D**




**(TOTAL FOR QUESTION 11 = 1 MARK)**

**(Questions continue on next page)**

12 **Benzene is nitrated using a mixture of concentrated nitric and sulfuric acids.**

**In this reaction, the concentrated sulfuric acid acts as**

☐ **A** an acid and catalyst.

☐ **B** an acid and nucleophile.

☐ **C** a base and catalyst.

☐ **D** a base and electrophile.

**(TOTAL FOR QUESTION 12 = 1 MARK)**

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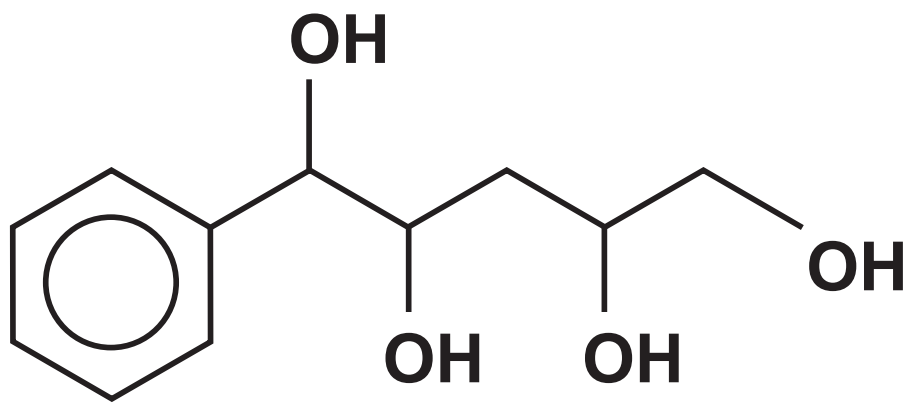
**(Questions continue on next page)**

**13** How many chiral carbon atoms are there in the following structure?




- ☐ **A** 2
- ☐ **B** 3
- ☐ **C** 4
- ☐ **D** 5

**(TOTAL FOR QUESTION 13 = 1 MARK)**

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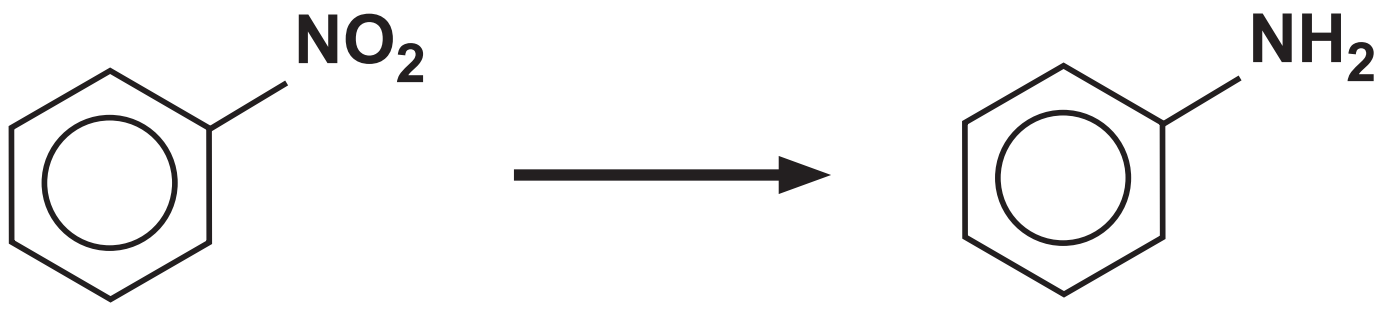
**(Questions continue on next page)**

**14** A sample of phenylamine was prepared from 2·46 g of nitrobenzene. The yield of phenylamine was 70·0% by mass.




nitrobenzene $M_r = 123$

phenylamine $M_r = 93$

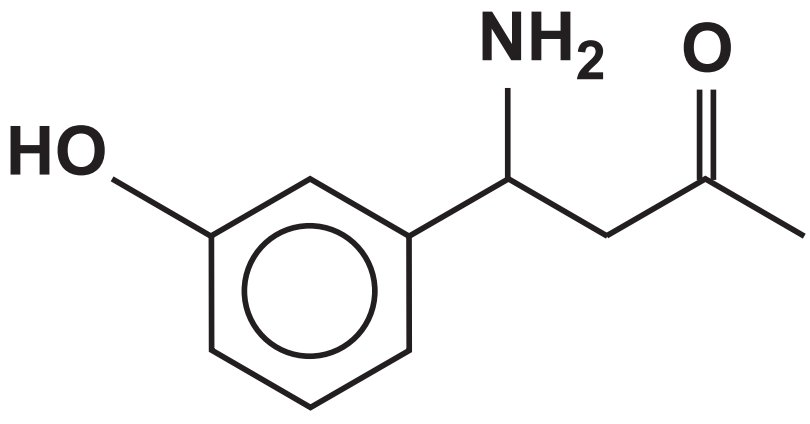
The mass of phenylamine produced is

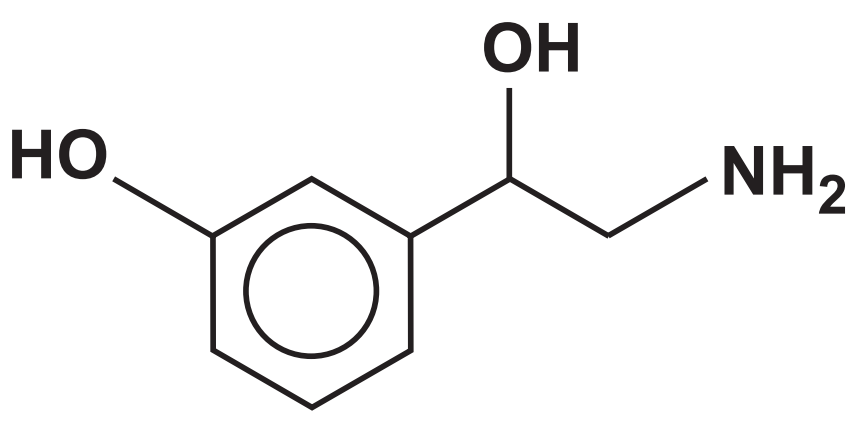
- ☐ A 0·014 g
- ☐ B 1·302 g
- ☐ C 1·722 g
- ☐ D 2·277 g

**(TOTAL FOR QUESTION 14 = 1 MARK)**

(Questions continue on next page)

**15 Which reagent can be used to distinguish between these two compounds?**




- ☐ **A** Bromine water
- ☐ **B** Copper(II) sulfate solution
- ☐ **C** Iodine in alkali
- ☐ **D** Tollens' reagent

**(TOTAL FOR QUESTION 15 = 1 MARK)**

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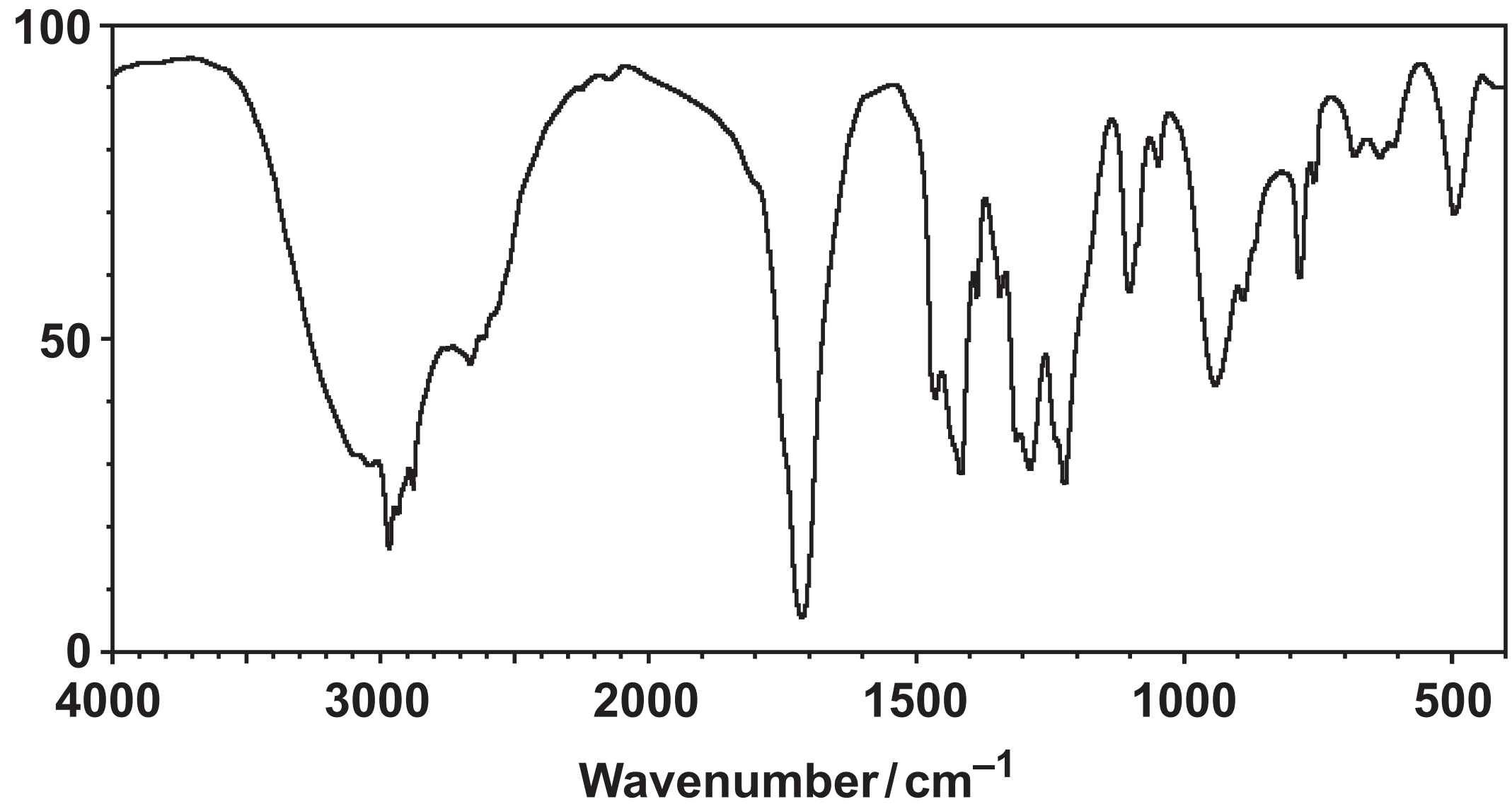
**(Questions continue on next page)**

**16 Which compound would give the infrared spectrum shown?**




(Question continues on next page)



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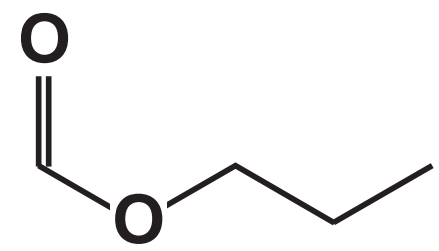
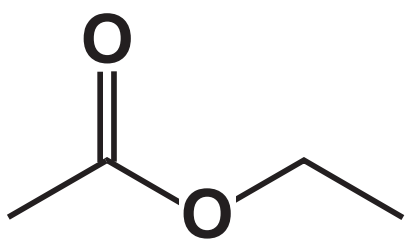
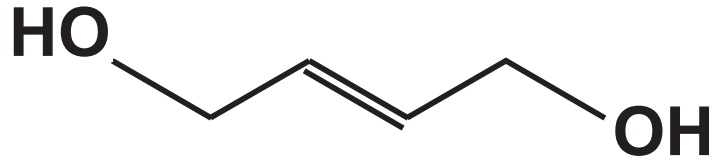
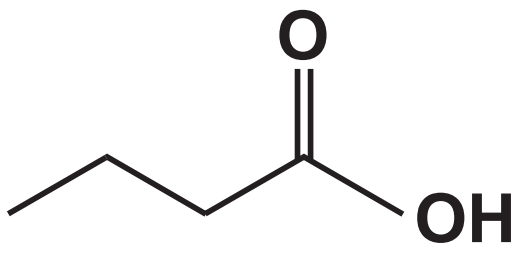
☐ A 

☐ B 

☐ C 

☐ D 

**(TOTAL FOR QUESTION 16 = 1 MARK)**

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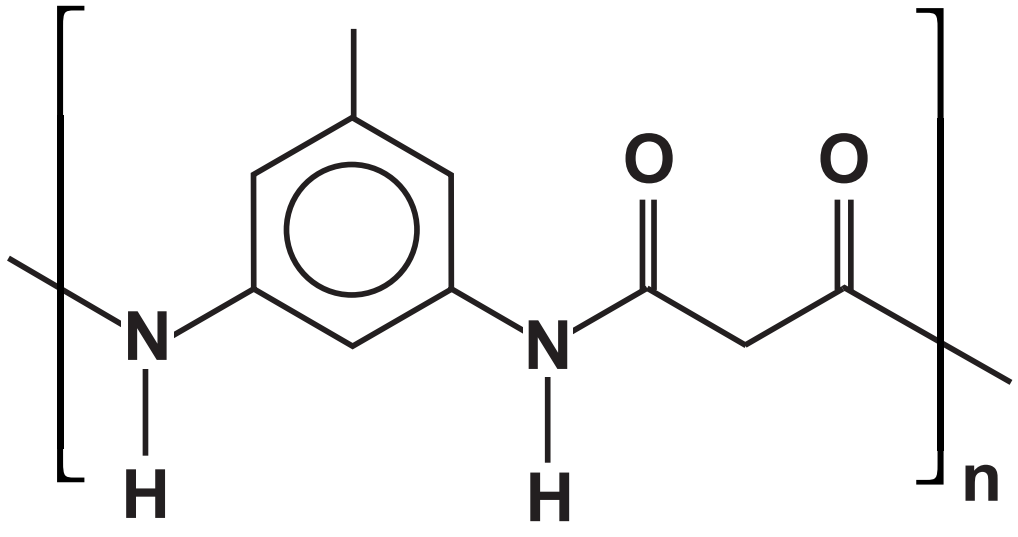
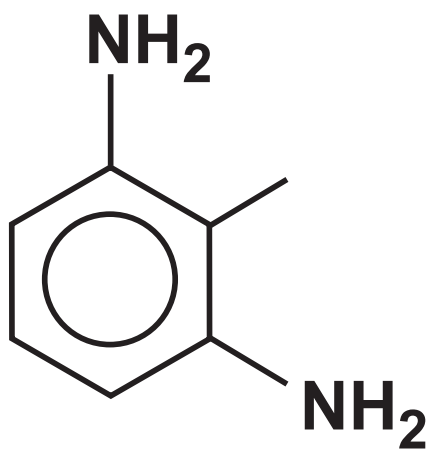
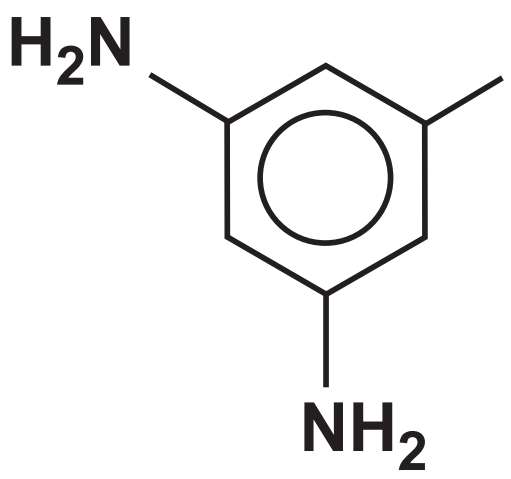
**(Questions continue on next page)**

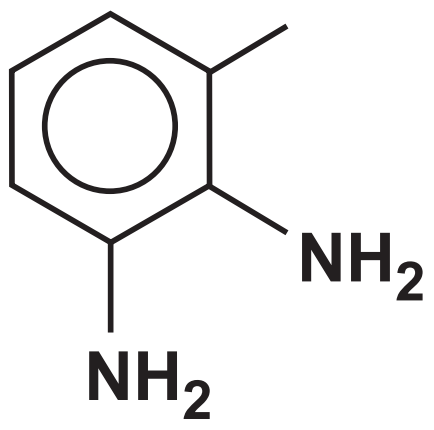
17 Which isomer reacts with propanedioyl dichloride to form the polymer shown?

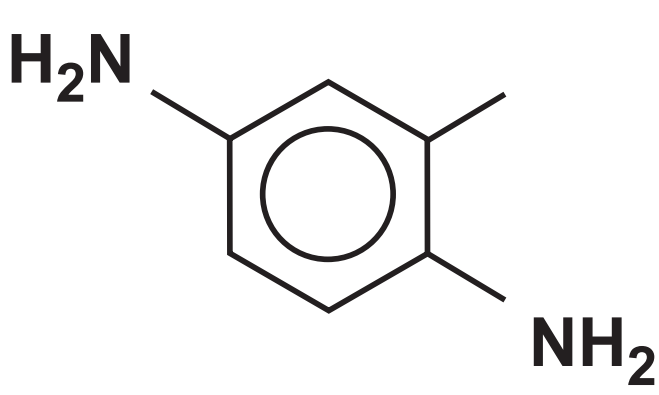



(Question continues on next page)

☐ A 


☐ B 


☐ C 


☐ D 


**(TOTAL FOR QUESTION 17 = 1 MARK)**

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**(Questions continue on next page)**

18 Benzaldehyde, $C_6H_5CHO$, reacts with an aqueous solution of potassium hydroxide.

During this reaction, the benzaldehyde is both oxidised and reduced.

The organic products of this reaction are

☐ A $C_6H_5COOH$ and $C_6H_5CH_2OH$

☐ B $C_6H_5COOH$ and $C_6H_5CH_2O^-K^+$

☐ C $C_6H_5COO^-K^+$ and $C_6H_5CH_2OH$

☐ D $C_6H_5COO^-K^+$ and $C_6H_5CH_2O^-K^+$

**(TOTAL FOR QUESTION 18 = 1 MARK)**

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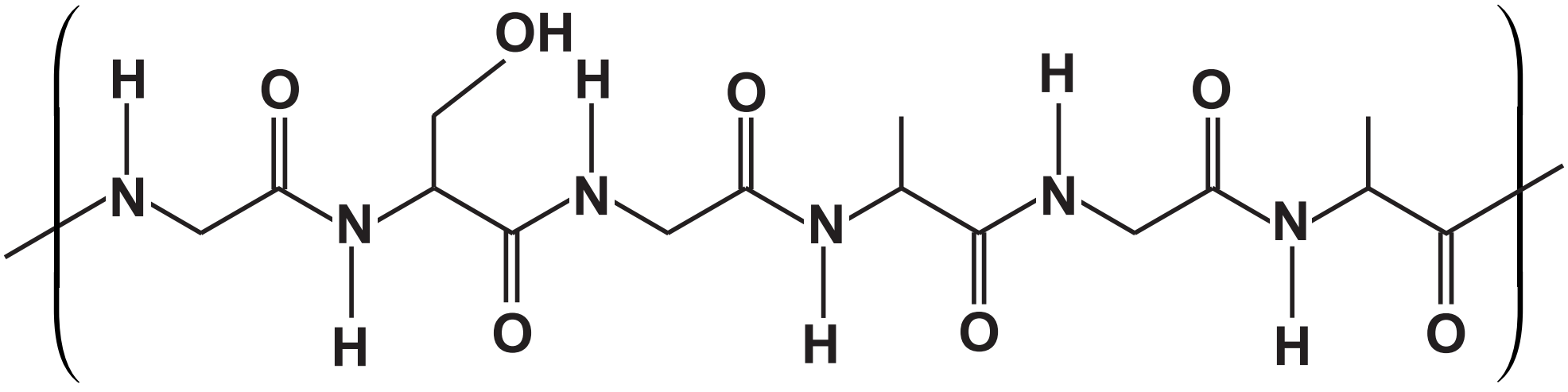
(Questions continue on next page)

19 Fibroin is one of the proteins in silk. Part of the structure of fibroin is shown.




How many DIFFERENT amino acids have combined to form this part of the structure?

☐ A 2

☐ B 3

☐ C 4

☐ D 6

(TOTAL FOR QUESTION 19 = 1 MARK)

TOTAL FOR SECTION A = 20 MARKS

(Section B begins on next page)

## SECTION B

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

**20 Chromium forms many different complex ions.**

**(a) State and explain the shape of the $[CrCl_4]^-$ complex ion. (2 marks)**

**Shape** _____

**Explanation**

**(Question continues on next page)**

(b) When a small amount of aqueous sodium hydroxide is added to a solution of chromium(III) ions, $[Cr(H_2O)_6]^{3+}(aq)$, a green precipitate forms.

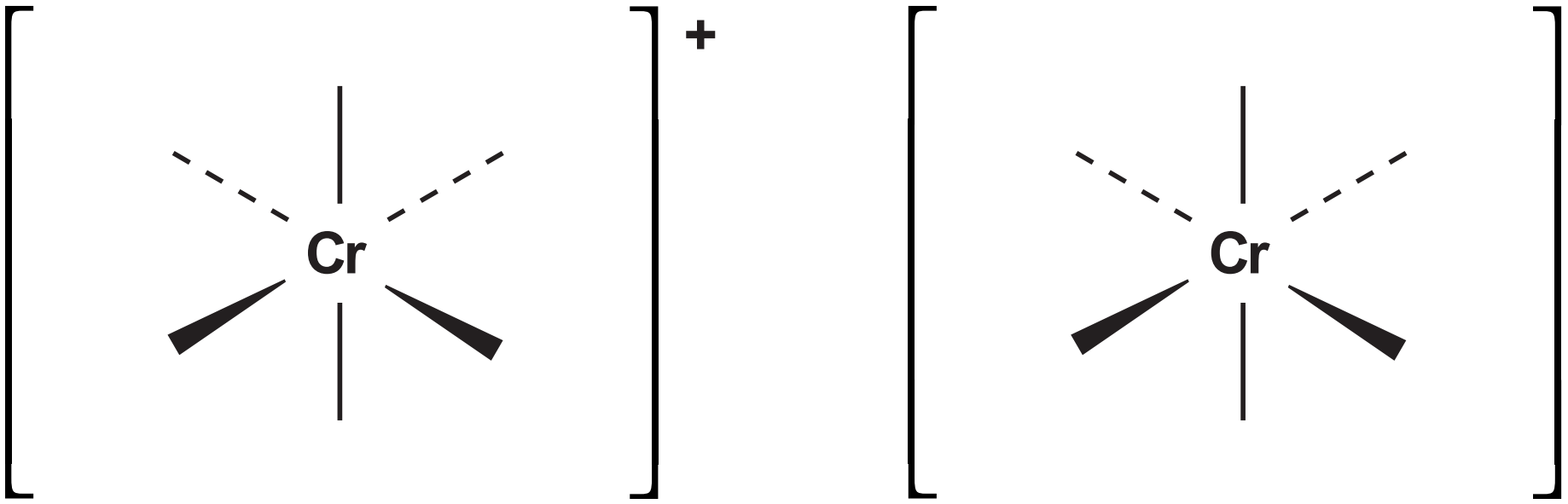
This precipitate dissolves in excess aqueous sodium hydroxide.

Write the ionic equations for these two reactions. Include state symbols. (2 marks)

(Question continues on next page)

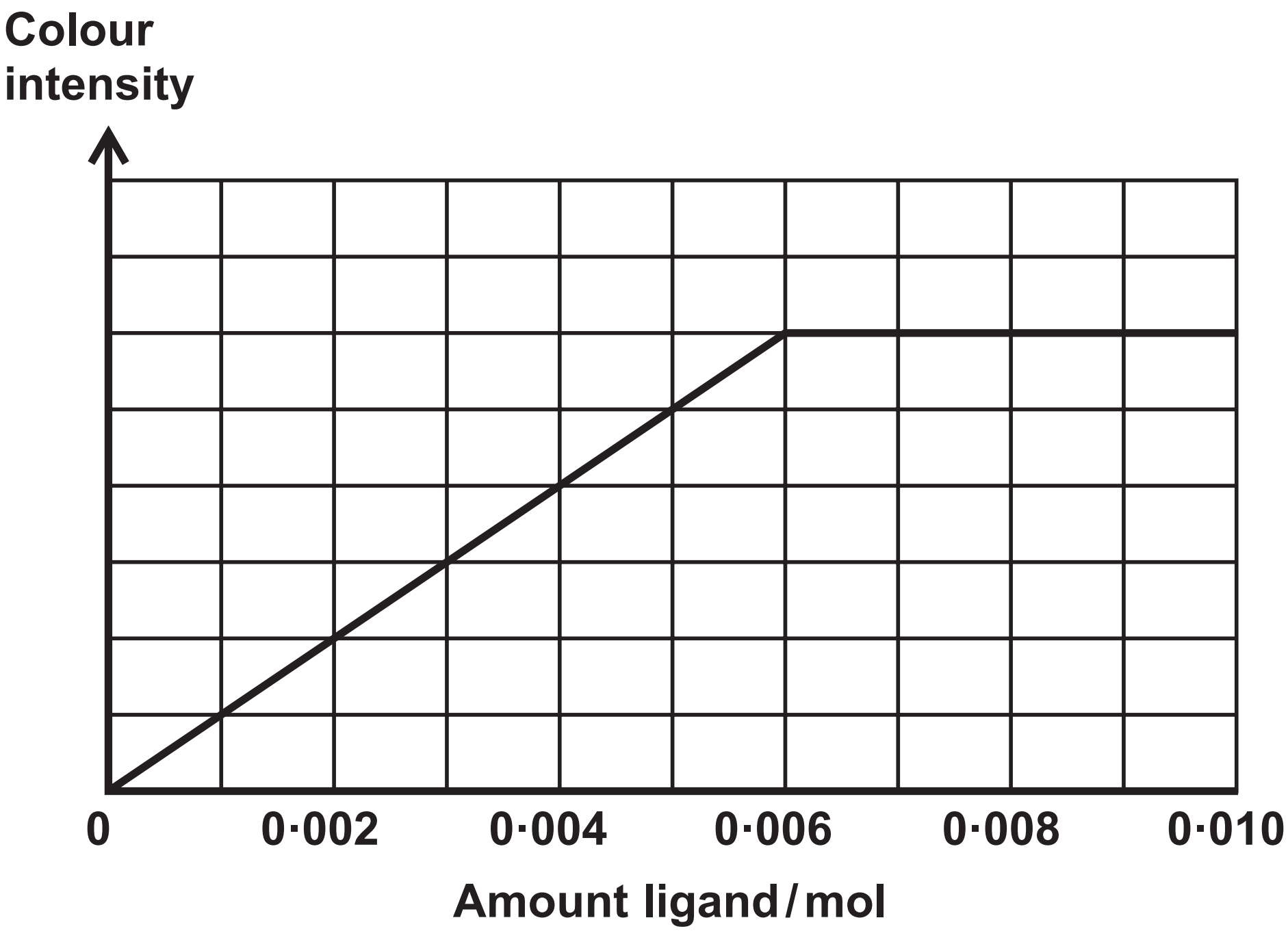
(c) The complex ion $[Cr(NH_3)_4Cl_2]^+$ is octahedral and exists as two isomers.

Complete the diagrams to show these two isomers. (2 marks)




(Question continues on next page)

(d) The diagram shows how the colour intensity of an aqueous solution containing 0·001 mol of chromium(III) ions varies with increasing amounts of cyanide ions, $CN^-$.



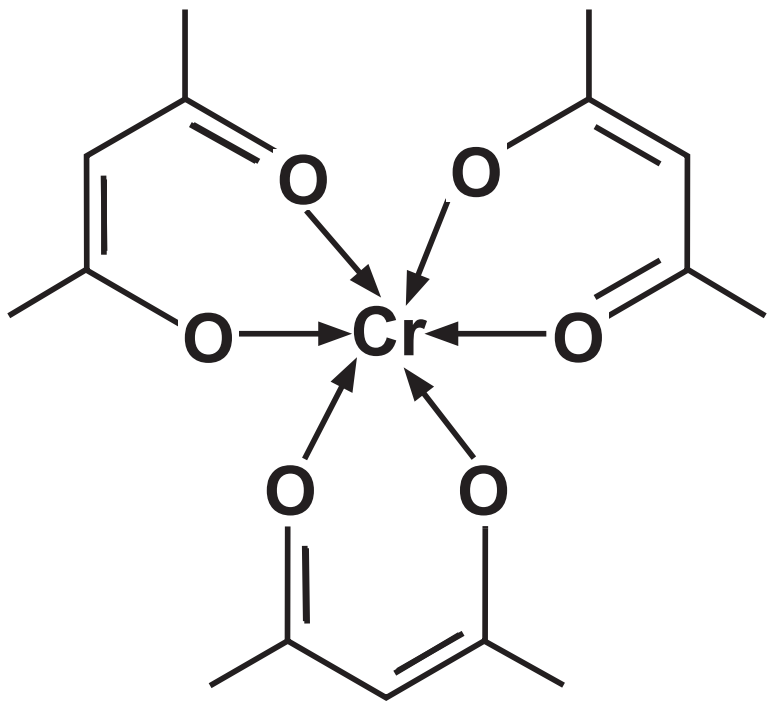

Chromium(III) ions form a complex ion with EDTA with a greater colour intensity than the complex ion formed with cyanide ions.

Sketch on the above axes the result you would expect to obtain if increasing amounts of EDTA were used instead of $CN^-$. (2 marks)

(Question continues on next page)

(e) **Chromium(III) ions form a NEUTRAL complex with the bidentate ligand commonly known as ‘acac’.**

**The structure of the chromium(III) complex $Cr(acac)_3$ is**




**On page 29 draw the structure of the bidentate ligand ‘acac’. (1 mark)**

**(Answer on next page)**

**(TOTAL FOR QUESTION 20 = 9 MARKS)**

**(Questions continue on next page)**

21 The –OH group is present in alcohols and phenols.

(a) Phenol, $C_6H_5OH$, is used as a starting material to make polymers, explosives and drugs.

(i) State what is SEEN when phenol reacts with excess bromine water. (1 mark)

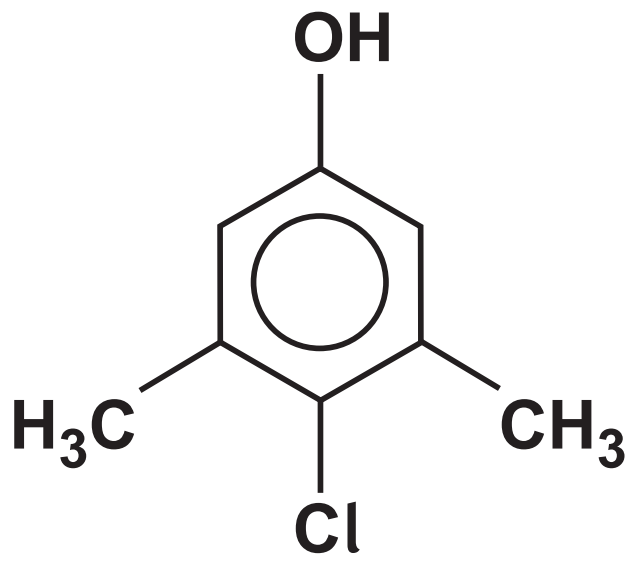
(ii) Write the equation for the reaction between phenol and excess bromine water. State symbols are not required. (2 marks)

(Question continues on next page)

*(iii) Benzene only reacts with bromine in the presence of a Friedel-Crafts catalyst. Explain why bromine reacts much more readily with phenol than with benzene. (2 marks)

(Question continues on next page)

(iv) Compound P is a powerful antiseptic.




Give the systematic name of compound P.
(1 mark)

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*(b) Phenol is more acidic than aliphatic alcohols, such as ethanol, but less acidic than carboxylic acids. It reacts with sodium hydroxide but not with sodium carbonate.

2·5 g of a mixture of phenol and benzoic acid, $C_6H_5COOH$, was added to excess sodium carbonate solution, $Na_2CO_3$. 185 $cm^3$ of carbon dioxide was produced.

$$2C_6H_5COOH + Na_2CO_3 \longrightarrow 2C_6H_5COONa + H_2O + CO_2$$

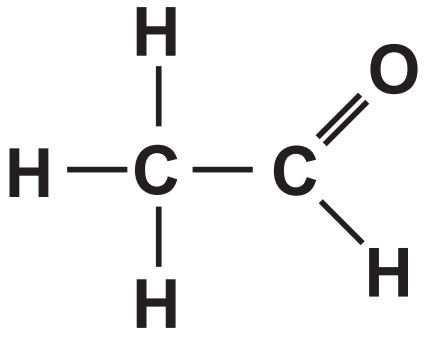
Calculate the percentage by mass of phenol in the mixture.

(The volume of 1 mol of gas under the conditions of the experiment is 24 000 $cm^3$) (4 marks)

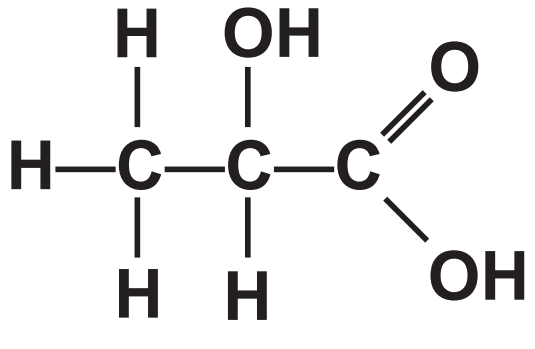
(Answer on next page)

(Question continues on next page)

(c) Lactic acid (2-hydroxypropanoic acid) is used as a flavouring. It may be prepared from ethanal.



ethanal



lactic acid

(i) Devise a two-step synthesis to produce lactic acid from ethanal. Include the reagents and conditions for each step, and the structure of the intermediate compound. (3 marks)

(Continue your answer on next page)

(ii) State the number of peaks in the LOW resolution proton nmr spectrum of lactic acid. (1 mark)

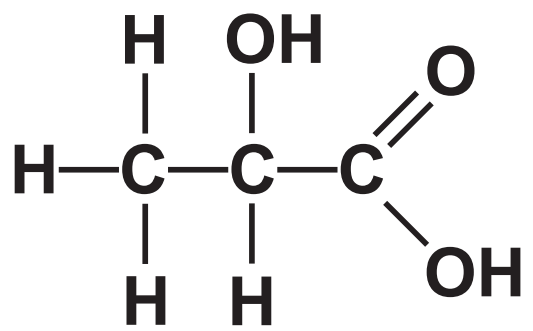
(iii) The hydrogen of the alcohol group in lactic acid produces a single peak in the proton nmr spectrum.

Give the chemical shift you would expect for this peak. (1 mark)

(Question continues on next page)

(iv) **Two molecules of lactic acid react to form one molecule of a cyclic di-ester.**

**The structure of lactic acid is shown below**

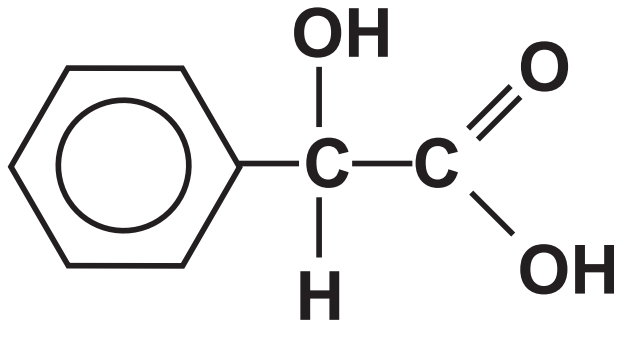



**On page 37 draw the structure of the cyclic di-ester. (1 mark)**

**(Answer on next page)**

(Question continues on next page)

(d) 2-hydroxy-2-phenylethanoic acid is more commonly known as mandelic acid. It has antibacterial properties.




(i) Mandelic acid is made when 2-chloro-2-phenylethanoic acid reacts with hydroxide ions.

Draw the $S_N1$ mechanism for this reaction. (3 marks)

(Question continues on next page)

*(ii) Explain why the mandelic acid, produced by the $S_N1$ mechanism from a single optical isomer of 2-chloro-2-phenylethanoic acid, is NOT optically active. (3 marks)

(Question continues on next page)

(iii) An impure sample of mandelic acid can be recrystallised using methanol as the solvent.

The steps of the recrystallisation are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in capital letters. (5 marks)

Step 1 The sample was dissolved in the MINIMUM amount of hot methanol.

(Question continues on next page)

**Step 2 The HOT solution was FILTERED.**

**Step 3 The filtrate was cooled in an ICE BATH.**

**(Question continues on next page)**

**Step 4 The mixture was FILTERED using suction filtration.**

**(TOTAL FOR QUESTION 21 = 27 MARKS)**

**(Questions continue on next page)**

**22 This question is about some metals and their compounds.**

**(a) Potassium and copper form ions with a single positive charge. Some information about these metals is given in the table.**

| | Potassium | Copper |
|---|---|---|
| Electronic configuration | $[Ar]4s^1$ | $[Ar]3d^{10}4s^1$ |
| Metallic radius / nm | 0·235 | 0·128 |

(Question continues on next page)

(i) Most transition metals in Period 4 have two electrons in the 4s orbital of their atoms. State why copper atoms have one electron in their 4s orbitals. (1 mark)

(Question continues on next page)

(ii) Copper atoms have more electrons than potassium atoms. Explain why the metallic radius of copper is smaller than that of potassium. (1 mark)

(Question continues on next page)

(b) The standard electrode potential of the copper(II) / copper half-cell is $E^{\ominus} = +0{\cdot}34$ V.

$$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$$

The effect of changing the concentration of the ions is calculated using the equation

$$E = E^{\ominus} + \frac{RT}{96\,500 \times n} \ln [Cu^{2+}(aq)]$$

where n is the number of electrons in the half-equation, T is the temperature in kelvin and R is the gas constant.

Calculate the electrode potential of the half-cell at 298 K when the concentration of copper(II) ions is $0{\cdot}100\,mol\,dm^{-3}$. (2 marks)

[Gas constant, $R = 8{\cdot}31\,J\,mol^{-1}\,K^{-1}$]

(Continue your answer on next page)

(Question continues on next page)

(c) An aqueous solution of copper(II) ions reacts with excess iodide ions to form a white precipitate of copper(I) iodide.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

(i) The relevant standard electrode potentials are given.

$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$ $\quad E^{\ominus} = +0{\cdot}15\,V$

$I_2(aq) + 2e^{-} \rightleftharpoons 2I^{-}(aq)$ $\quad E^{\ominus} = +0{\cdot}54\,V$

Calculate the value for $E^{\ominus}_{cell}$ for the reaction between copper(II) ions and iodide ions and suggest why the reaction takes place. (3 marks)

(Continue your answer on next page)

(Question continues on next page)

(ii) Many coins are made of alloys containing copper and other metals.

A coin was treated with concentrated nitric acid to convert all the copper atoms into copper(II) ions. The solution was neutralised, made up to 1·00 $dm^3$ and mixed thoroughly. Excess potassium iodide was added to 25·0 $cm^3$ portions of this solution and the liberated iodine was titrated with sodium thiosulfate solution of concentration 0·150 $mol\,dm^{-3}$.

The mean titre was 10·90 $cm^3$.

The equations for the reactions are

$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$$

(Question continues on next page)

**Calculate the mass of copper in the coin.**
**Give your answer to THREE significant figures.**
**(4 marks)**

**(Question continues on next page)**

(d) Silver and gold are below copper in the Periodic Table.

(i) The standard electrode potential values involving silver ions are given.

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^\ominus = +0{\cdot}80\,V$

$Ag^{2+}(aq) + e^- \rightleftharpoons Ag^+(aq)$ $\quad E^\ominus = +1{\cdot}98\,V$

Write the equation for the reaction involving these species that is thermodynamically feasible under standard conditions. Explain whether or not this reaction is a disproportionation. (2 marks)

(Question continues on next page)

(ii) Chloroauric acid, $HAuCl_4$, is used in the production of gold nanoparticles. It is formed when gold reacts with aqua regia, a mixture of concentrated nitric and hydrochloric acids.

$$Au + HNO_3 + 4HCl \rightleftharpoons HAuCl_4 + NO + 2H_2O$$

Explain, in terms of oxidation numbers, why this is a redox reaction. (2 marks)

**(TOTAL FOR QUESTION 22 = 15 MARKS)**

**TOTAL FOR SECTION B = 51 MARKS**

(Section C begins on next page)

## SECTION C

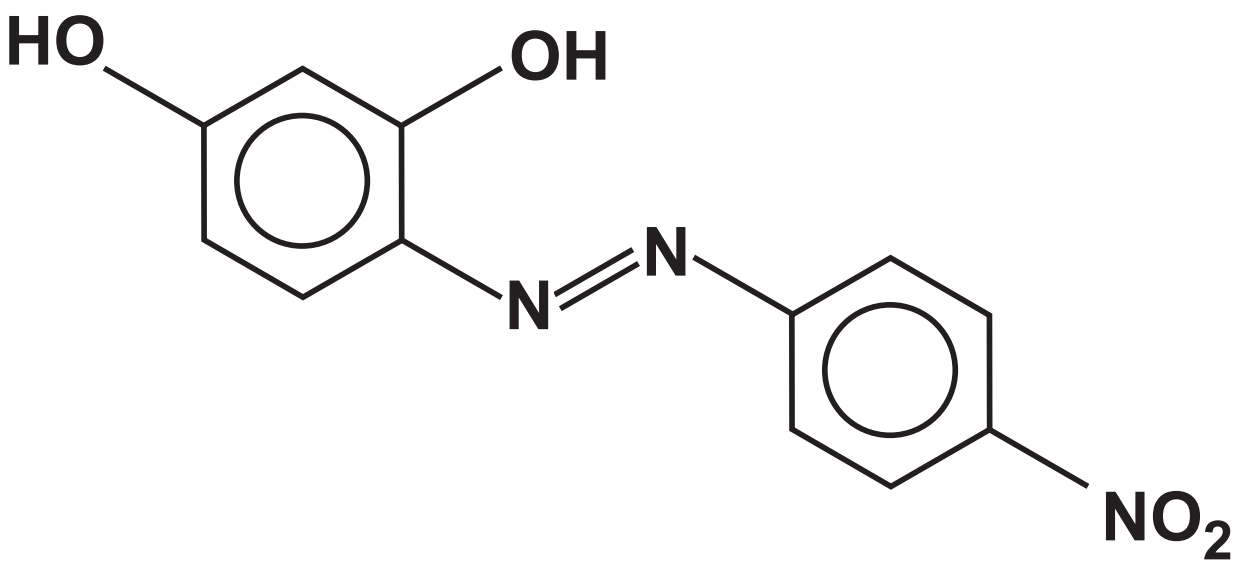
**Answer ALL the questions. Write your answers in the spaces provided.**

**23**

## ORGANIC NITROGEN COMPOUNDS

**Nitrogen is present in many organic compounds, including amines, amides and nitriles. Many useful products are made from these compounds.**

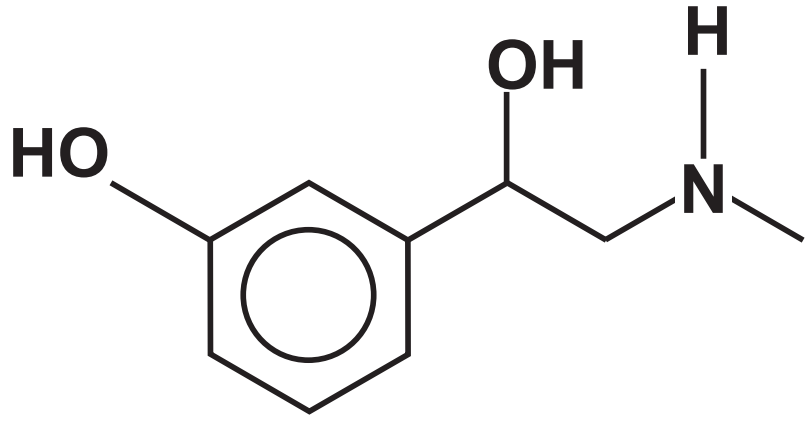
**Amines are used to make dyes, drugs and polymers. Phenylamine and other aromatic amines are used to manufacture azo dyes such as azo violet.**




**azo violet**

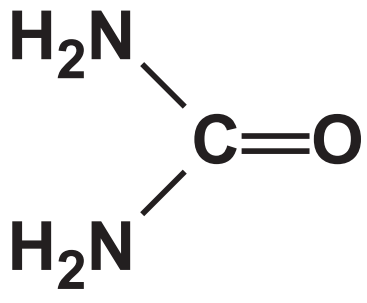
**(Question continues on next page)**

The drug phenylephrine is used as a decongestant.



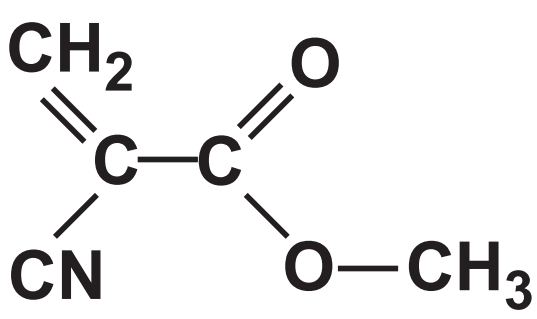

phenylephrine

Urea is a white crystalline solid which is soluble in water. It is used as a fertiliser as well as in the manufacture of biuret (used to test for compounds containing a peptide linkage) and of drugs such as barbiturates.




urea

Methyl 2-cyanopropenoate is the main component of superglue.

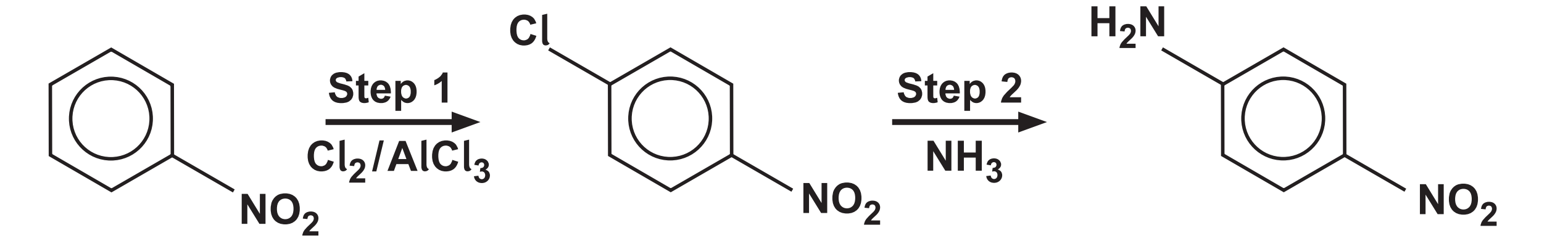



methyl 2-cyanopropenoate

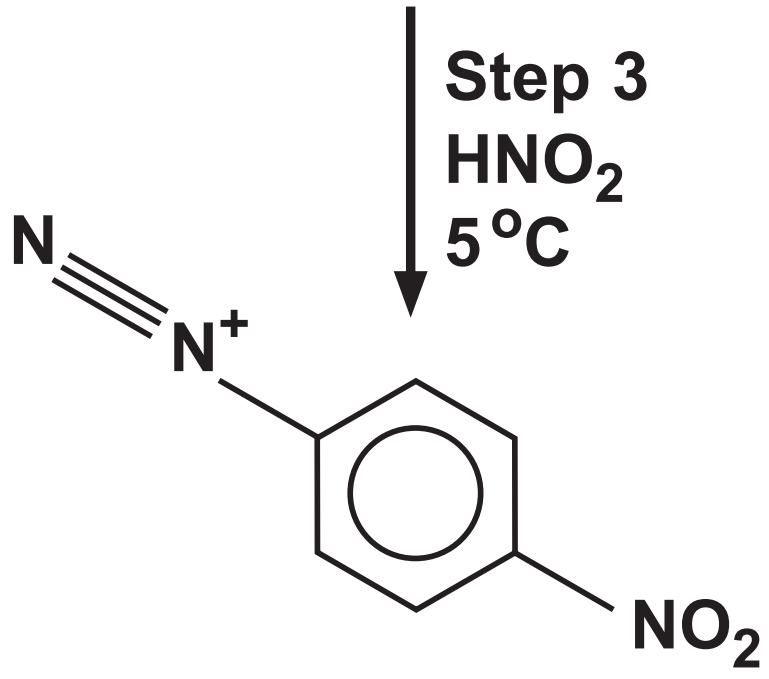
It polymerises rapidly in the presence of water.

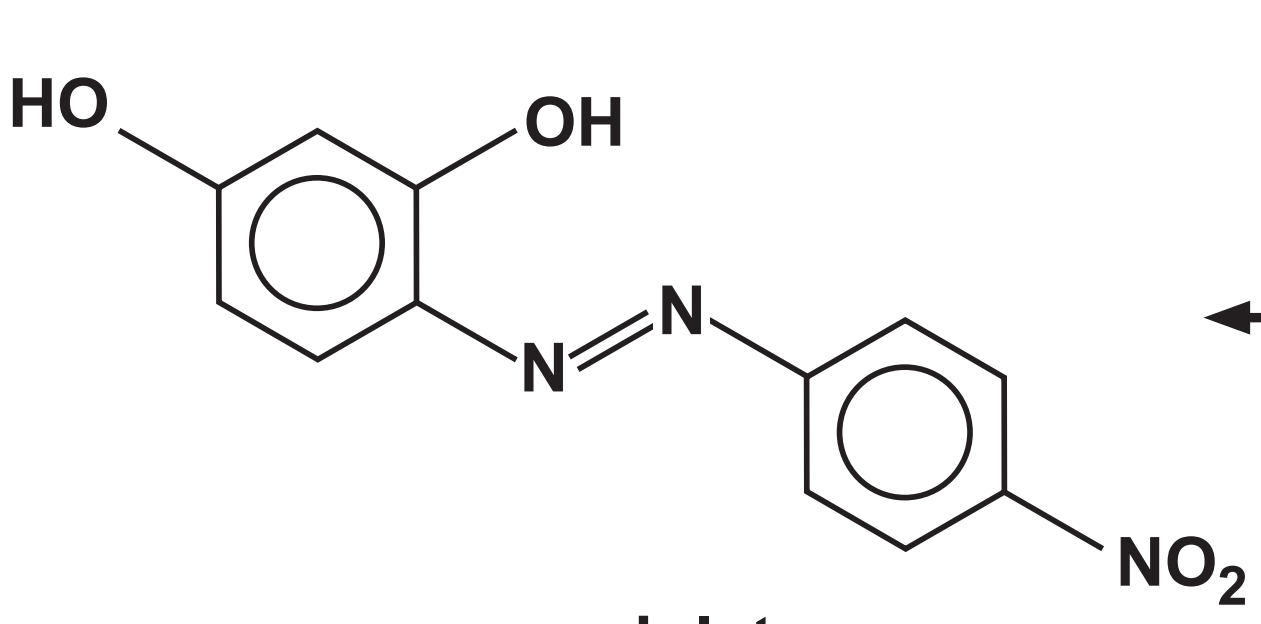
(Question continues on next page)

**(a) Azo violet is synthesised from nitrobenzene in four steps.**




**1-chloro-4-nitrobenzene** **1-amino-4-nitrobenzene**




**azo violet**

**(Question continues on next page)**

(i) Give the mechanism for the formation of 1-chloro-4-nitrobenzene from nitrobenzene. Include an equation to show the formation of the electrophile. (4 marks)

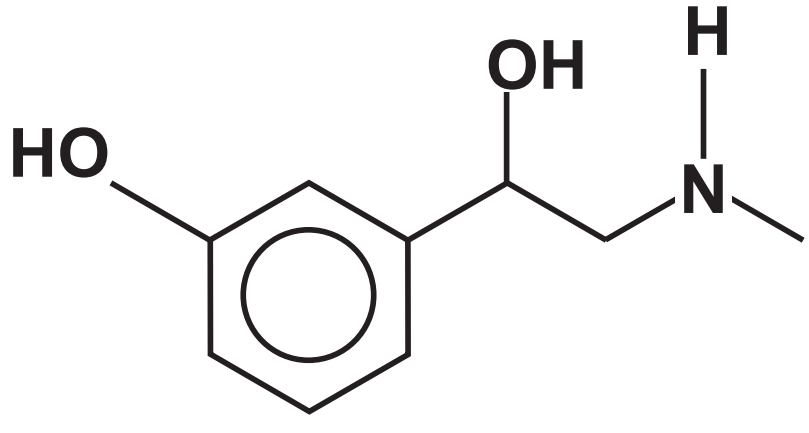
(Question continues on next page)

(ii) Draw the structure of the organic species needed for Step 4. (1 mark)

(iii) Give the molecular formula for azo violet. (1 mark)

(Question continues on next page)

(b) Draw the structure of the product formed when phenylephrine reacts with EXCESS ethanoyl chloride. (2 marks)




phenylephrine

(Question continues on next page)

(c) (i) Suggest, with the aid of a diagram, why urea, $(H_2N)_2CO$, is soluble in water. (3 marks)

(ii) Urea is made by reacting ammonia and carbon dioxide at 200 °C and 200 atm pressure.

Write the equation for this reaction. State symbols are not required. (1 mark)

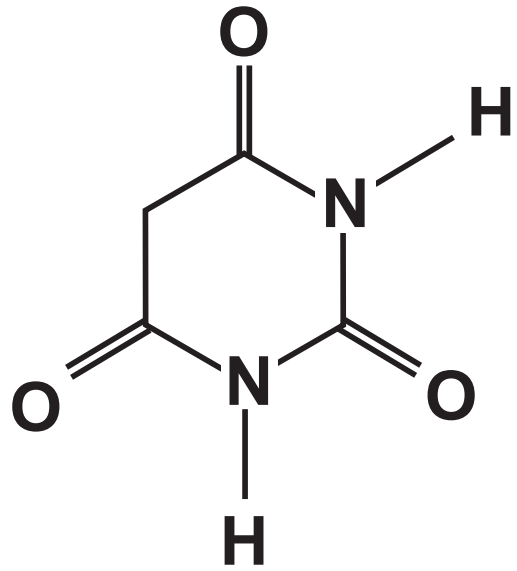
(Question continues on next page)

(iii) **Biuret is formed when urea is heated above its melting temperature. A molecule of biuret is made when two molecules of urea react together with the loss of ammonia.**

**Suggest the DISPLAYED formula of a molecule of biuret. (1 mark)**

**(Question continues on next page)**

(iv) **Barbiturate drugs are derivatives of barbituric acid.**




**barbituric acid**

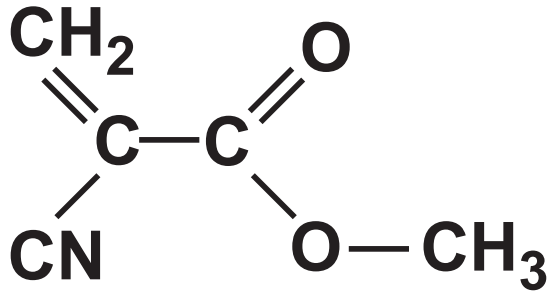
**Barbituric acid is formed from urea and a dicarboxylic acid in a condensation reaction.**

**On page 63 draw the SKELETAL formula of the dicarboxylic acid. (1 mark)**

**(Answer on next page)**

(Question continues on next page)

(d) (i) NAME the functional groups present in methyl 2-cyanopropenoate. (2 marks)




(ii) Methyl 2-cyanopropenoate polymerises.

On page 65 name the type of polymerisation and draw TWO repeat units of the polymer. (3 marks)

(Answer on next page)

**Type** _____

**(TOTAL FOR QUESTION 23 = 19 MARKS)**

**TOTAL FOR SECTION C = 19 MARKS**

**TOTAL FOR PAPER = 90 MARKS**

**END**