NAME _____ CLASS **21S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2022

CHEMISTRY **9729/03**

Higher 2 **19 September 2022**

Paper 3 Free Response Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at end of this booklet. The question number must be clearly shown.

Answer all questions in Section A.
Answer 1 question in Section B.

The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**21**
2	**20**
3	**19**
4 or 5	**20**
Penalty (delete accordingly)	
Lack **3sf** in final answer	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	**80**

This document consists of **31** printed pages inclusive of 1 blank page.

Section **A**
Answer **all** the questions in this section.

For Examiner's use

1 **(a)** Bromoethane reacts with "acetylide" anion, $CH_3C{\equiv}C:^-$ to form new carbon−carbon bonds. This reaction takes place in two steps.

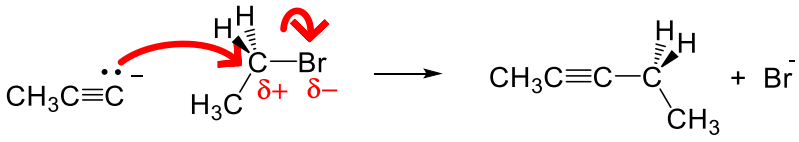
In step 1, an acid-base reaction occurs. $CH_3C{\equiv}C:^-$ is formed from the reaction of propyne and a strong base, sodium amide, $NaNH_2$.

step 1: $CH_3C{\equiv}CH + :NH_2^- \rightarrow CH_3C{\equiv}C:^- + NH_3$

In step 2, the intermediate anion reacts with bromoethane to form the product.

step 2: $CH_3CH_2Br + CH_3C{\equiv}C:^- \rightarrow CH_3CH_2C{\equiv}CCH_3 + Br^-$
Name and suggest the mechanism for **step 2**. Show relevant dipoles, using curly arrows to indicate the movement of electron pairs.

Type of mechanism: nucleophilic substitution



[3]

(b) 4-bromopentanol can be used to synthesise Compound **C** by the three-step route shown in Fig. 1.1.

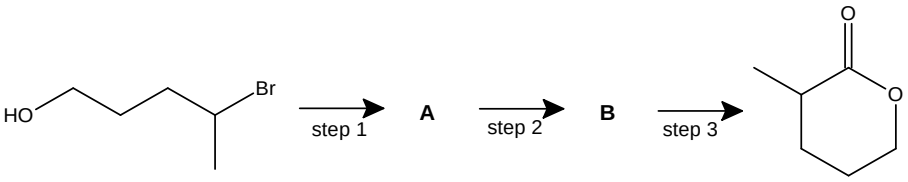
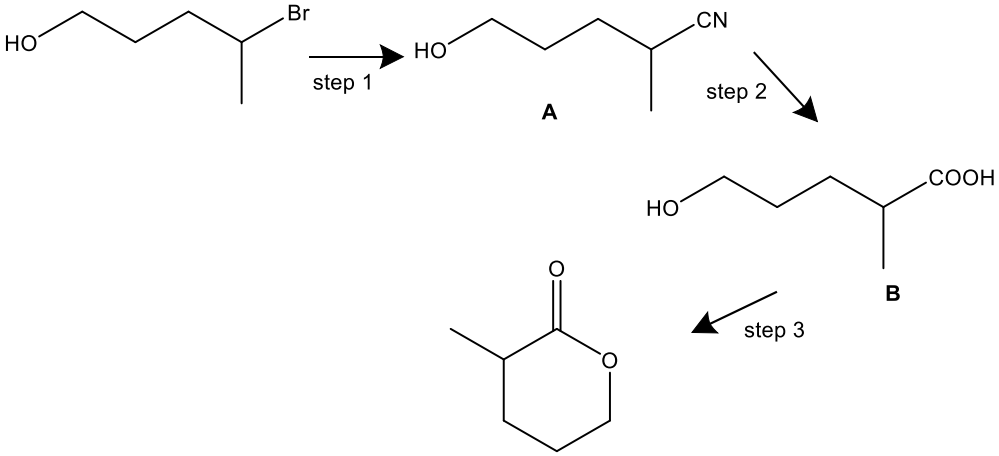


Fig. 1.1

State the structures for compounds **A** and **B**, and reagents and conditions for steps 1, 2 and 3 in this route. [4]



step 1 : NaCN (or KCN), ethanol, heat (✓)
step 2 : H_2SO_4(aq) (or HC*l*(aq)), heat (✓)

step 3 : concentrated sulfuric acid, heat(✓)

(c) Describe and explain the relative ease of hydrolysis of the following three chlorine-containing compounds. [3]

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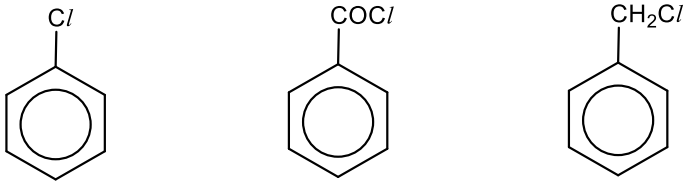


Ease of hydrolysis of C_6H_5Cl < $C_6H_5CH_2Cl$ < C_6H_5COCl

C_6H_5Cl is inert or unreactive to hydrolysis as the p–p orbital overlap results in the delocalisation of lone pair of electrons on Cl atom of C_6H_5Cl into the π–electrons system of benzene ring, leading to the formation of partial double bond character of C–Cl bond and hence, strengthening C–Cl bond.

Thus, C_6H_5Cl is resistant towards nucleophilic attack.

C_6H_5COCl is most readily hydrolysed because the C of –COCl is highly electron–deficient or has the highest partial positive charge as it is bonded to two electronegative atoms, O and Cl. Hence, C_6H_5COCl is more susceptible towards nucleophilic attack than $C_6H_5CH_2Cl$.

(d) Ethanol is formed when bromoethane is heated with NaOH(aq).
The standard enthalpy change of combustion of ethanol is –1367 kJ mol^{-1}.
In an experiment, 0.23 g of ethanol was burned under a container, using a spirit lamp. An unknown mass of water was heated from 30 °C to its boiling point. The process was found to be 70 % efficient.
Calculate the mass of water that could be brought to the boiling point by burning this amount of ethanol.
[Given specific heat capacity of water is 4.18 J g^{-1} K^{-1}] [2]

Amount of ethanol burnt = $\frac{0.23}{46.0}$ = 5.00×10^{-3} mol

Heat evolved by combustion of ethanol = $5.00 \times 10^{-3} \times 1367$ =6.835 kJ

Heat absorbed by x g of water
= 70/100 x $5.00 \times 10^{-3} \times 1367$
= 4.78 kJ mass of water, $x = 4.78 \times 10^3 / (4.18 \times 70)$ = 16.3 g

(e) **(i)** Nitrosyl bromide, Br-N=O is an inorganic halogen-containing compound. It decomposes to NO and Br_2 as shown below. [2]

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g), \quad \Delta H_r$$

Given that the bond energy of N−Br is +120 kJ mol^{-1}, use appropriate bond energy data from the *Data Booklet* to calculate the enthalpy change of decomposition of nitrosyl bromide.

(ii) Enthalpy changes of formation of NOBr(g) and NO(g) and the enthalpy change of vaporisation of $Br_2(l)$ are given below. [3]

ΔH_f (NOBr(g))	y kJ mol^{-1}
ΔH_f (NO(g))	+90 kJ mol^{-1}
$\Delta H_{vap}(Br_2(l))$	+31 kJ mol^{-1}

With the aid of an energy cycle, use your answer in **(i)** and the given data to calculate the enthalpy change of formation of NOBr(g).

(e) **(i)** 2 O=N–Br(g) → 2 N=O(g) + Br–Br(g), $\Delta H_r = 2 \times \Delta H_{decomposition}$(NOBr)

ΔH_r = +2*E*(N=O) + 2*E*(N–Br) – 2*E*(N=O) – *E*(Br−Br)

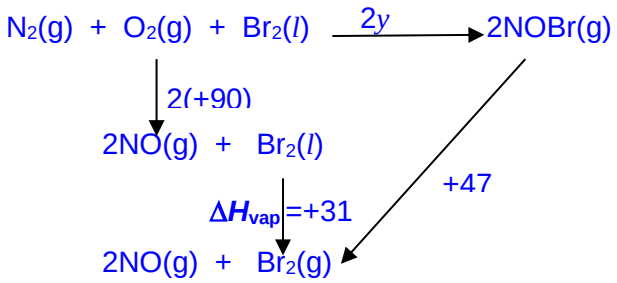
= 2*E*(N–Br) – *E*(Br−Br)

= 2(+120) – (+193) |

= +47 kJ mol^{-1}

$\Delta H_{decomposition}$ (NOBr) = ½ (+47) = +23.5 kJ mol^{-1}

(ii)



By *Hess*' Law,

2*y* = 2(+90) + (+31) – (+47)

y = ΔH_f(NOBr) = +82.0 kJ mol^{-1}

(f) **(i)** State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant $E^{\ominus}$ values. [2]

(ii) Describe a reaction that illustrates the relative oxidising abilities of two halogens of your choice. [1]

(iii) Iodine and chlorine react together to form solid iodine trichloride, ICl_3. Given the following enthalpy changes, calculate the standard enthalpy change of formation of ICl_3(s).

$I_2(g) + 3Cl_2(g) \rightarrow 2ICl_3(s)$	$\Delta H^{\ominus} = -214$ kJ mol^{-1}
$I_2(s) \rightarrow I_2(g)$	$\Delta H^{\ominus} = +38$ kJ mol^{-1}

[1]

(f) (i) Down the group, $E^{\ominus}(X_2/X^-)$ becomes less positive, implying that the tendency of X_2 to be reduced decreases. [2]

Hence, the oxidising power of X_2 decreases down the group.

(ii) Eg. $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

(Halogen displacement reaction where the stronger oxidising halogen can oxidise the halides of the weaker oxidising halogen. or

Eg. $Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$

Reaction of X_2 with Fe^{2+}

(iii) *Let x* = $\Delta H_f^{\ominus} ICl_3$(s)

$\Delta H^{\ominus} = \sum \Delta H^{\ominus}_f$ products − $\sum \Delta H^{\ominus}_f$ reactants

-214= 2x -3(+38)

x = $\Delta H_f^{\ominus} ICl_3$(s) = -88.0 kJ mol^{-1}

[Total: 21]

2 **(a)** Explain why transition element complexes are usually coloured.

For Examiner's Use

The presence of ligands causes the d orbitals to split into 2 different energy levels with a small energy gap.

Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital which is partially filled.

Hence, transition element complexes are coloured and the colour observed is the complement of the colours absorbed.

(b) In a given electroplating experiment, a solution of $CrCl_3$(aq) is electrolysed using a current of 3.50 A. Calculate the time, in min, required to produce 4.60 g of chromium by this electrolysis. [2]

Amount of Cr = 4.60 / 52.0 = 0.0885 mol

Cathode: $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

$Q = n_eF = It$

Hence $Q = 3 \times 0.0885 \times 96500$

$= 25621$ C

Time taken = 25621 / 3.50 = 7320s = 122 min

(c) The half reaction involving conversion of ethanol to ethanoic acid is given below:

$$CH_3COOH(aq) + 4H^+(aq) + 4e^- \rightleftharpoons C_2H_5OH(aq) + H_2O(l) \quad E^{\ominus}=+0.58V$$

(i) Using *Data Booklet* and the above information, draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the CH_3COOH/ C_2H_5OH half-cell. Indicate the direction of movement of electrons in the external circuit when the cell is operating**.** [3]

(ii) The amount of ethanol in a person's breath is measured with a breathalyzer.

C_2H_5OH is oxidised to CH_3COOH and potassium dichromate, $K_2Cr_2O_7$ is reduced to Cr^{3+} in acidic medium. The colour change observed is orange to green.

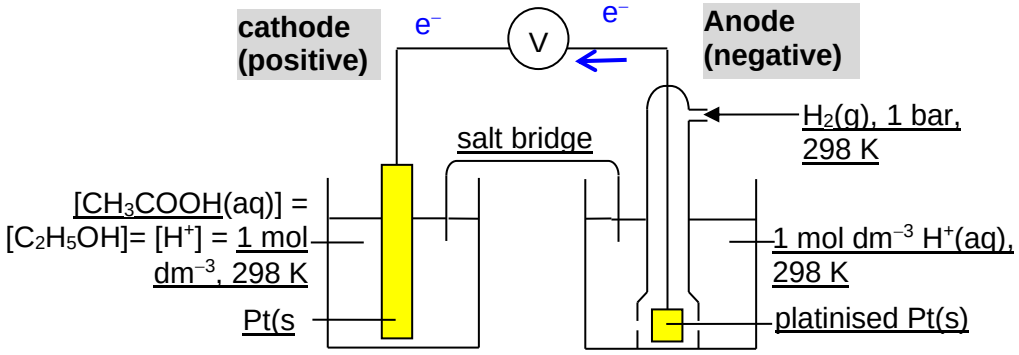
Calculate $E^{\ominus}_{cell}$ for the above reaction. [1]

(iii) Using the $E^{\ominus}_{cell}$ calculated in **(c)(ii)**, calculate $\Delta G^{\ominus}$, with units, for the cell reaction. [1]

(iv) State and explain how the e.m.f. of the cell would change if HC*l*(aq) is added to the cathode half-cell in **(c)(ii)**.

[2]

(c) (i) $CH_3COOH(aq) + 4H^+(aq) + 4e^- \rightleftharpoons C_2H_5OH(aq) + H_2O(l)$ $E^{\ominus}=+0.58V$



(ii) $E^{\ominus}_{cell}$ = (+1.33) – (+0.58) = +0.75 V [1m]

(iii) Overall: $2Cr_2O_7^{2-} + 3C_2H_5OH + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$

$\Delta^{\ominus}G = -nFE$

n = 12

$\Delta^{\ominus}G$= −12 x 96500 x (+0.65) = −753 000 J mol^{-1} ≈ −753 kJ mol^{-1}

(iv) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^{\ominus}_{cathode}$ = +1.23 V

- When H^+ is added, $[H^+]$ will increase (✓).
- By Le Chatelier's Principle, the equilibrium position will shift to the right (✓), so as to remove some $[H^+]$ to re-establish equilibrium.
- $E_{cathode}$ becomes more positive(✓)
- Since $E_{cell} = E_{cathode} - E_{anode}$, thus E_{cell} will become more positive (✓).

(d) A solution of XeF_2 is a strong oxidising agent. A solution containing 25.0 g dm^{-3} of XeF_2 is reacted with another solution containing 0.150 mol dm^{-3} of a Cr(III) salt. In an experiment, 15.20 cm^3 of the XeF_2 solution is required to completely react with 10.0 cm^3 of the Cr(III) solution. XeF_2 is reduced to Xe in the reaction. Determine the final oxidation state of Cr after the reaction. [3]

Amount of $XeF_2 = \frac{15.2}{1000} \times \frac{25}{169}$ = 0.002249 mol

XeF_2 is reduced to Xe and oxidation state of Xe changes from +2 to 0.

Amount of electrons transferred = 2 × 0.002249 = 0.004497 mol

Amount of Cr(III) = $\frac{10}{1000} \times 0.150$ = 0.00150 mol

Amount of electrons lost from 1 mol of Cr(III) = $\frac{0.004497}{0.00150}$ = 3 mol

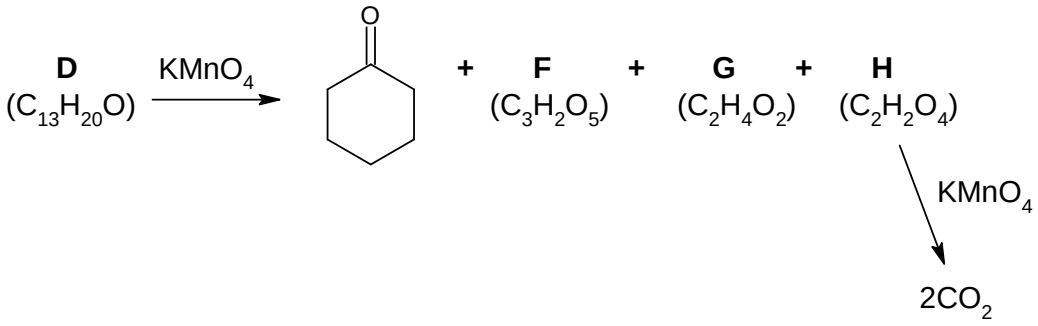
∴ oxidation state of Cr increases by 3 units

∴ oxidation state of Cr is +6 after reaction.

(e) Hot acidified $KMnO_4$ oxidises several classes or organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds

can be determined. Some compounds are easily oxidized while others require longer heating.

The following scheme shows the reaction with hot acidified $KMnO_4$, of compound **D** and its oxidation products.



- Compound **D** effervesces with sodium metal. **D** also reacts with hot acidified potassium dichromate(VI) to give **compound** $C_{13}H_{18}O$**.**
- Compound **F** gives an orange precipitate with 2,4-dinitrophenyhydrazine.
- Both compounds **F** and **H** dissolve in NaOH(aq).

(i) Explain these observations. [2]

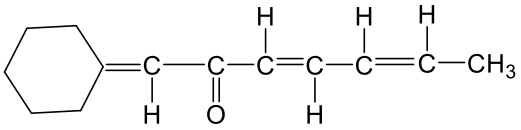
D undergoes redox reaction with Na and oxidation with warm acidified potassium dichromate(VI). D contains secondary alcohol.

F undergoes condensation with 2,4-DNPH to give orange ppt. F contains ketone.

F and H undergo acid-base reaction with NaOH(aq). F and H contain carboxylic acid.

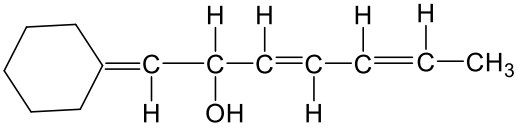
(ii) Suggest the structures of compounds **D**, **F** and **G**. [3]

$C_{13}H_{18}O$**:**

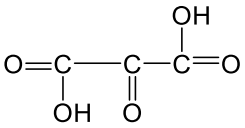


Note: Alkene is not oxidised by $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat

D



F



G CH_3COOH

[Total: 20]

3 Nitrogen is the most abundant element in our planet's atmosphere. The various nitrogen-containing organic compounds play an important role in our lives, as they serve as the building materials for amino acids, proteins and even in our DNA.

For Examiner's Use

(a) **Table 3.1** below shows some **aromatic** organic nitrogen compounds that have important uses in both chemical and pharmaceutical industries.

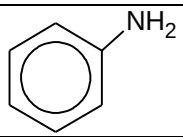
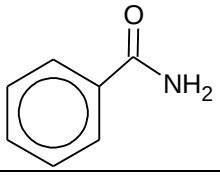
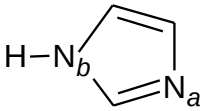
Name of compound	Structure	K_b
phenylamine		3.98×10^{-10}
benzamide		1.00×10^{-14}
imidazole		-

Table 3.1

(i) Using the data provided in Table 3.1, suggest an explanation for the difference in the relative basicities of phenylamine and benzamide. [2]

(ii) Based on the structure of a molecule of imidazole, suggest an explanation why nitrogen N_a would have a higher K_b value than N_b. [1]

(i) Phenylamine is a stronger base than benzamide because it has higher K_b. The lone pair on nitrogen in benzamide is delocalised completely over C=O through p-p orbital and due to the electronegative oxygen atom hence it is totally not available (✓) to be donated to a proton/H^+.

(ii) N_a has higher $K_{b\ value}$ because:
The lone pair on N_a atom is in the sp^2 hybrid orbital which is not delocalised OR not in the same plane as the π electron cloud / p-orbitals of the carbon atoms in the molecule. As such, the lone pair is not delocalised and is more available to be donated to a proton/H^+.
OR
p-p overlap between the orbitals of N_b and the π electron cloud / p-orbitals of the carbon atoms results in the delocalisation of the lone pair on N_b, reduces its availability to donate to acid/ H^+.

(b) Amino acids are sometimes referred to as the "building blocks of life". In human beings, there are 20 amino acids that are used to manufacture the proteins required by the body.

One such essential α-amino acid is histidine, that is required to maintain good mental and physical states of the human body. Food sources such as fish, poultry and nuts are good sources of histidine.

(i) In terms of bonding, explain why histidine has a much higher melting point than 4-nitrophenylamine, despite having similar M_r in Table 3.2

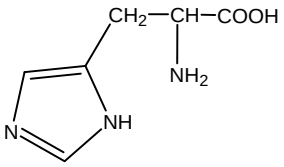
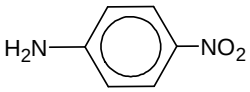
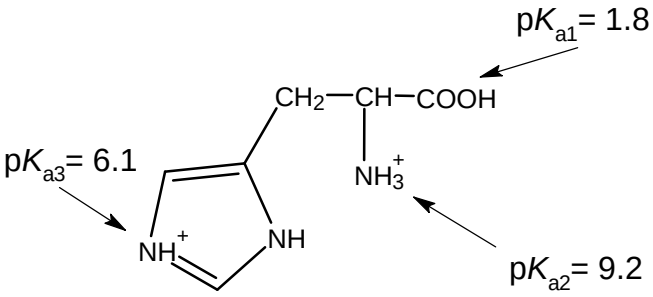
compound	Structure	melting point/ ^oC
histidine		285
4-nitrophenylamine		146

Table 3.2

[2]

(ii) The diagram below shows the protonated form of histidine, which can be represented by H_3A, and the respective acid dissociation constants for its three acidic groups.



Predict the structure of the major species that would be present when histidine is placed into buffer solutions with the following pH values:

- pH = 7
- pH = 12

[2]

For Examiner's Use

(iii) A chemist invented two new enzymes:

- "histidinase-C" that can hydrolyse at the C-terminal of the histidine (His) amino acid residue;
- "lysinase-N" that can hydrolyse at the N-terminal of the lysine (Lys) amino acid residue;

A polypeptide chain from a liver protein consists of a total of 11 amino acids. This polypeptide was subjected to partial hydrolysis by these two enzymes separately, and the following fragments were obtained.

Amino acid fragments obtained with histidinase-C:	Amino acid fragments obtained with lysinase-N:
Ala-Lys-Ser-His	Lys-Cys-His
Ser-Lys-His	Lys-Ser-His-Ser
Ser-Lys-Cys-His	Ser
	Lys-His-Ala

Table 3.3

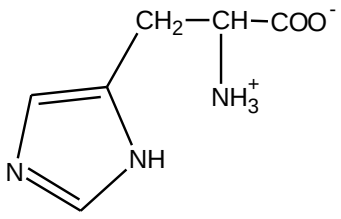
Using the above information, deduce the correct sequence of the 11 amino acid residues in the polypeptide chain. [2]

(i) Histidine exists as zwitterions in the solid state, which are held by stronger electrostatic forces of attraction / ionic bonds, while molecules of 4-nitrophenylamine are held by weaker hydrogen bonds.

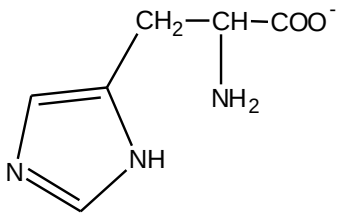
More energy is required to overcome the stronger ionic bonds between the zwitterions of histidine.

(ii)

- pH = 7



- pH = 12



(iii) *Working:*
Find the "head" of the polypeptide: Ser appears on both columns in the table.
Find the "tail" of the polypeptide:His appears on both columns in the table.
Hence, Ser-2-3-4-5-6-7-8-9-10-His
Using histidinase-C:
Ser-Lys-His
Ala-Lys-Ser-His
Ser-Lys-Cys-His
Using lysinase-C:
Ser
Lys-His-Ala
Lys-Ser-His-Ser
Lys-Cys-His

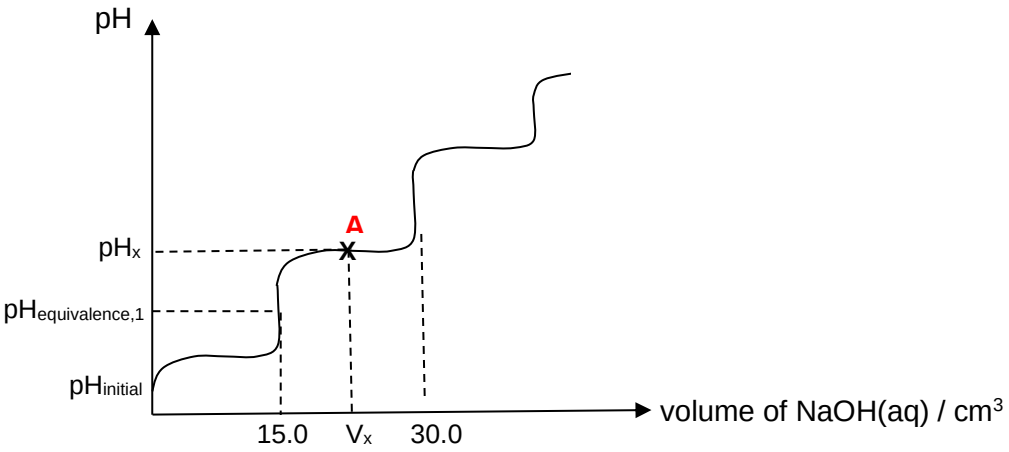
Ser-Lys-His-Ala-Lys-Ser-His-Ser-Lys-Cys-His

(c) *Information from **2(b)(ii)** would be useful for this part of the question.*

Intrigued by his newly found knowledge on amino acids after completing his SLS lesson on Organic Nitrogen Compounds, a H2 Chemistry student from Jurong Pioneer JC decided to seek help from his chemistry tutor to conduct a more in-depth analysis.

He prepared a fresh sample containing 15.0 cm^3 of 0.100 mol dm^{-3} fully protonated histidine and titrated it against 0.100 mol dm^{-3} NaOH(aq).

The following graph was obtained:



(i) Calculate the initial pH of the 0.100 mol dm^{-3} fully protonated histidine, $pH_{initial}$. (Ignore the effect of pK_{a2} and pK_{a3} on the pH). [1]

(ii) An amphiprotic species is one that is able to donate and accept a proton. The pH of a solution containing an amphiprotic species is given by the following expression.

$$pH = \tfrac{1}{2}(pK_1 + pK_2)$$

In the titration above, an amphiprotic species is formed at the first equivalence point, when 15.0 cm^3 of NaOH(aq) was added to the sample of protonated histidine.

Calculate the pH of the amphiprotic species formed at the first equivalence point and draw its structure. [2]

(iii) Using your answer to **3(c)(ii)** and information from Table 3.4 given below, choose the best indicator to detect the 1st end-point of the titration. Briefly explain your answer.

indicator	**thymol blue**	**methyl yellow**	**methyl red**
pK_a	1.7	3.1	5.2

[1]

Table 3.4

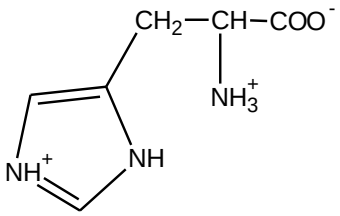
(iv) Point **A** on the titration graph represents a solution of maximum buffering capacity that is equally effective in removing small amounts of H^+ and OH^- ions added.

State the value of $\mathbf{V_x}$, the volume of NaOH(aq) added and the value of $\mathbf{pH_x}$, at point **A**. [2]

(i) $pK_{a1} = 1.8$
$K_a = 10^{-1.8}$

$K_a = 10^{-1.8} = x^2 / (0.100 - x) \approx x^2 / 0.100$
Solving, $x = [H^+] = 0.03981$ mol dm^{-3}
$pH_{initial} = -\lg(0.03981) = 1.40$

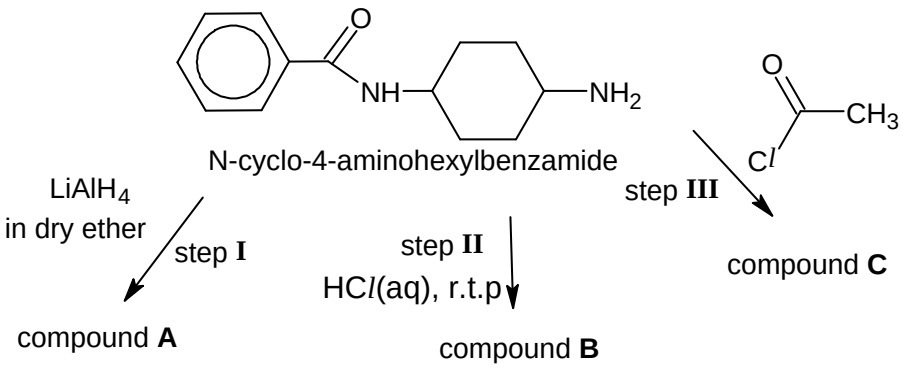
(ii) $pH \approx (pK_{a1} + pK_{a2}) / 2 = (1.8 + 6.1) / 2 = 3.95$ or 4.0



(iii) The best indicator would be methyl yellow.
Working range of indicators: p$K_a \pm 1$
Hence, the working range for methyl orange is between 2.1 to 4.1, which coincides with the pH at the first equivalence point.

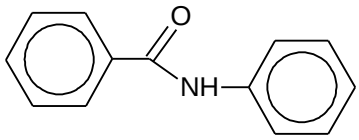
(iv) Volume at 1st equivalence point = 15.0 cm^3
Volume at 2nd equivalence point = 30.0 cm^3
$V_x = (15.0 + 30.0) / 2 = 22.50$cm^3

(d) The diagram below shows some reactions involving *N*-cyclo-4-amino hexylbenzamide.



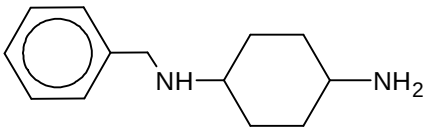
(i) Give the structures of compounds **A, B** and **C**. [3]

(ii) Suggest a simple chemical test that could be used to distinguish between *N*-cyclohexylbenzamide and *N*-phenylbenzamide.

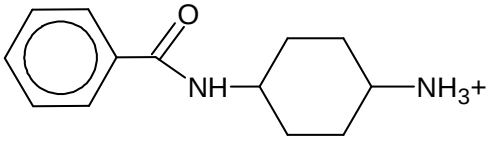


N-phenylbenzamide [2]

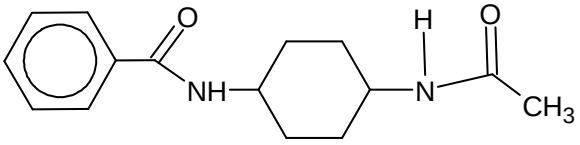
(i) **A:**



B:



C:



[Total: 20]

Section B

Answer one question from this section.

For Examiner's Use

4 **(a)** Phosphoryl chloride is a colourless liquid with the formula $POCl_3$.

Table 4.1 shows the electronegativity values of the atoms in $POCl_3$.

atom	electronegativity / pauling units
phosphorus	2.2
chlorine	3.0
oxygen	3.5

Table 4.1

(i) $POCl_3$ hydrolyses in moist air releasing phosphoric acid and fumes of hydrogen chloride. [1]

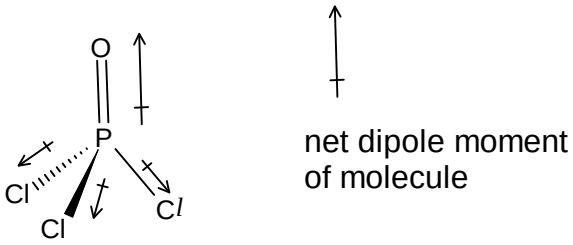
Write an equation to show the reaction of $POCl_3$ with water.

(ii) Draw the shape of $POCl_3$. [2]
Indicate clearly the polarity of each bond it contains, and its overall net polarity.

(iii) Predict all possible intermolecular forces which could exist between $POCl_3$ molecules. [2]
Explain how these forces arise.

(i) $\mathbf{POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl}$

(ii)



There are instantaneous dipole–induced dipole attractions (id–id) and permanent dipole–permanent dipole attractions (pd–pd) between phosgene molecules.

id–id attraction arises due to the constant motion of electrons, a molecule develops an instantaneous dipole within itself when its electrons are distributed unevenly instantaneously. This instantaneous dipole then induces a temporary dipole on another molecule close to it, giving rise to id–id

pd–pd attraction arises due to the electrostatic attraction between polar molecules which have permanent dipoles (or has net dipole moment within each molecule). [2]

(b) The boiling points of phosphorus trichloride, PCl_3 and nitrogen trichloride, NCl_3 are given below in Table 4.2.

At 373 K, both PCl_3 and NCl_3 exist as gases. Predict with reasons, which of the two gases will deviate more from ideal gas behavior.

compound	Formula	M_r	boiling point/ K
phosphorus trichloride	PCl_3	137.5	350
nitrogen trichloride	NCl_3	120.5	344

Table 4.2

[2]

Both phosphorus trichloride and nitrogen trichloride are simple molecular structures with net dipole moment.
1st mark:
However, phosphorus trichloride has a larger electron cloud/larger number of electrons which results in stronger intermolecular instantaneous dipole-induced dipole interactions.
OR
phosphorus trichloride has stronger pd-pd attractions between its molecules as P-Cl bond is more polar than N-Cl bond (difference in electronegativity between P and Cl is larger than that between N and Cl).

Phosphorus trichloride will show a greater relative deviation from ideality than nitrogen trichloride.

(c) **X**, **Y** and **Z** are Period 3 elements.
Element **X** forms a white oxide that is insoluble in water.
Element **Y** forms an oxide which forms a white precipitate when shaken with excess aqueous $Ba(NO_3)_2$ solution.
The oxide of element **X** dissolves when a solution of oxide of element **Y** is added to it.
Element **Z** forms an oxide that dissolves readily in water and the resulting solution turns moist red litmus blue.
The oxide of element **X** dissolves when a solution of oxide of element **Z** is added to it.
Identify the elements **Y**, **Z** and the oxide of **X** in the above reactions.

Write equations to account for the dissolution of the oxide of **X** in the two reactions above.

[4]

- Element Y: Sulfur
- Element Z: Sodium
- Oxide of Element X : Aluminium oxide or Al_2O_3
- white ppt correspond to $BaSO_4$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

$H_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2HNO_3(aq)$
White ppt

$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$

State symbols not required

(d) Dinitrogen tetroxide, N_2O_4, is a useful reagent in chemical synthesis. It forms an equilibrium mixture with nitrogen dioxide according to the equation below.

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

(i) At 318 K and 1 atm, the degree of dissociation of N_2O_4 is 37.8%.

Calculate the equilibrium constant, K_p. [2]

(ii) The degree of dissociation is found to be 28% when total pressure is increased.
Comment on why is there a difference in the degree of dissociation compared to **(d)(i)**. [1]

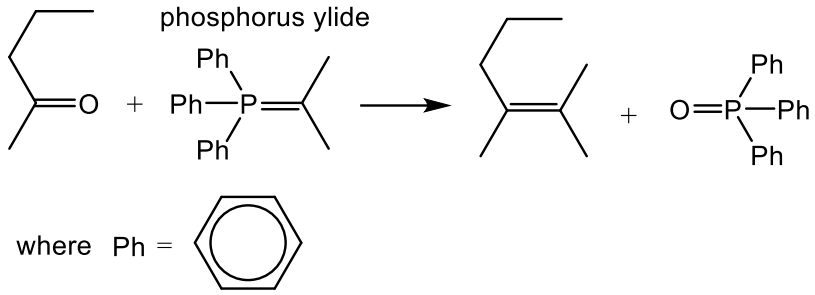
(i)

	$N_2O_4\,(g)$	⇌	$2NO_2\,(g)$
Initial amount/mol	1		0
Change in amount/ mol	-0.378		2 x 0.378
Equilibrium amount/ mol	0.622		0.756
Equilibrium pressure/atm	$\frac{0.622}{1.378} \times 1 = 0.451$		$\frac{0.756}{1.378} \times 1 = 0.549$

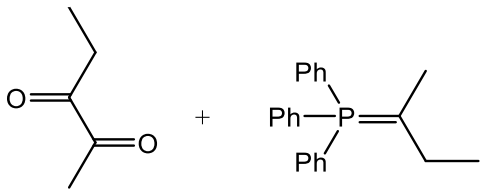
$$K_p = \frac{(0.549\ \text{atm})^2}{0.451\ \text{atm}} = \underline{0.668\ \text{atm}}$$

(ii) When pressure increase, the position of equilibrium shifts to the left to reduce the total no. of moles of gas in the system to decrease pressure which results in smaller degree of dissociation.

(e) A phosphorous ylide is used in the Wittig reaction which converts a carbonyl compound to an alkene. An example of a Wittig reaction is shown below.

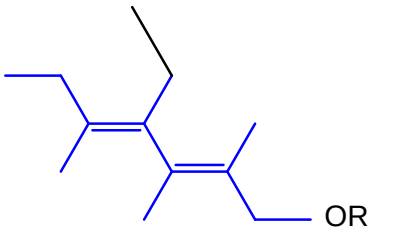


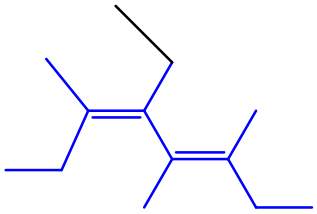
(i) Suggest the structure formed when 1 mole of the following carbonyl compound reacts with 2 moles of the phosphorous ylide via the Wittig reaction.



Hence, suggest the total number of stereoisomers that can be formed. [2]

The product formed:

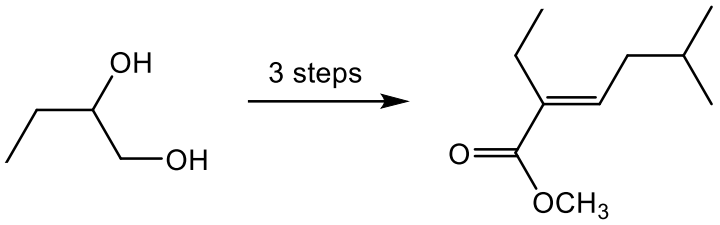




or other stereoisomer

Since the product has two C=C double bonds, total number of isomers formed $2^2 = 4$.

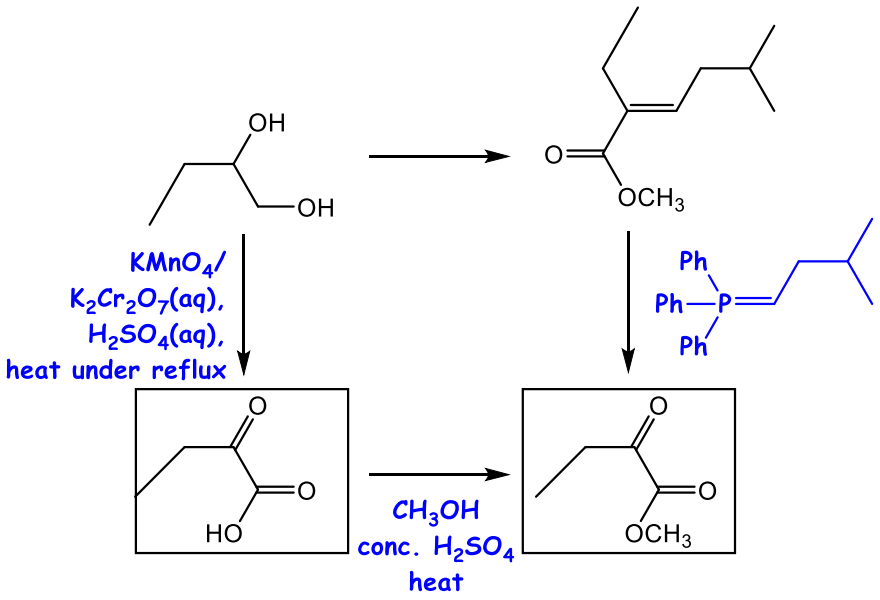
(ii) Using the Wittig reaction as one of the steps in a three-step synthesis route, suggest suitable reagents and conditions to synthesise compound **G** from butane-1,2-diol.



butane-1,2-diol compound **G**

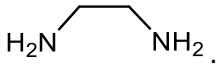
In your answer, include the structure of the intermediates formed.

In your answer, include the structure of the intermediates formed. [4]



For Examiner's comments

5 **(a)** The brown compound $[Fe(en)_pCl_q]Cl$ contains 19.8% Fe, 19.8% of N and 37.7% of Cl.

en is used to represent ethane-1,2-diamine  .

(i) ethane-1,2-diamine, *en*, is a *bidentate ligand*. What is meant by the term a *bidentate ligand*? [1]

(ii) Calculate the values of p and q and hence determine the formula of the brown compound. [2]

(iii) On treatment with water over a long period of time, it is converted to an orange complex, which has octahedral geometry.

Treatment of 0.01 mol of the product with excess aqueous $AgNO_3$ results in the precipitation of 4.31 g of AgCl.

Give the formula of the orange complex ion and suggest a balanced equation for its formation. [2]

(i) A *bidentate ligand* is an anion or neutral molecule that provides 2 lone pairs to form 2 dative bonds with central atom or ion. [1]

(ii) Let mass of the complex be 100 g.

	Fe	N	Cl
Mass / g	19.8	19.8	37.7
Amt / mol	0.3548	1.414	1.062
Relative amount/ mol	1	3.986	2.993
Simplest mole ratio	1	4	3

Since 1 en contains 2 N atoms, in 1 mole of brown compound, there are

4/2 = 2 en ligands

p = 2

Or in 1 mole of brown compound, there are 3 Cl^- in total

q +1 =3

q = 2

$[Fe(en)_2Cl_2]Cl$ is the brown compound. [2]

(iii) Amount of AgCl precipitated = 4.31 / (108 + 35.5) = 0.0300 mol

1 mol of the brown-orange complex ≡ 3 mol of free chloride ions (not dative bonded as ligands).

Formula of the brown-orange complex is $[Fe(en)_2(H_2O)_2]^{3+}$.

The treatment with water results in ligand exchange

$[Fe(en)_2Cl_2]^+ + 2H_2O \rightleftharpoons [Fe(en)_2(H_2O)_2]^{3+} + 2Cl^-$

[2]

(b) Brass is used to make window frames and other architectural models. Brass is a mixture of copper and zinc.

The process of etching brass involves dissolving the unprotected brass in aqueous iron (III) chloride until all the unwanted brass has been removed.

By using the relevant $E^{\ominus}$ values, explain if one or both components of the brass are soluble in aqueous iron (III) chloride.

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus}(Fe^{3+}/Fe^{2+}) = +0.77\ V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus}(Cu^{2+}/Cu) = +0.34\ V$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus}(Zn^{2+}/Zn) = -0.76\ V$

For the reaction between Cu and Fe^{3+}, $E^{\ominus}cell = +0.77 - 0.34 = +0.43V > 0$

For the reaction between Zn and Fe^{3+}, $E^{\ominus}cell = +0.77 - -0.76 = +1.53V > 0$

Both are spontaneous, as $E^{\ominus}cell > 0$, thus Fe^{3+} oxidises Cu to $Cu^{2+}(aq)$, Fe^{3+} oxidises Zn to $Zn^{2+}(aq)$, both metals dissolve forming metal ions.

[2]

(c) **(i)** Solid aluminium chloride, $AlCl_3$, may be produced by passing a stream of Cl_2 gas over heated Al metal in a long hard–glass tube.

The pH of 1.0 mol dm^{-3} solution of $AlCl_3$ in water is 3. Write equations where appropriate to account for the reactions of $AlCl_3$ in water**.** [1]

(ii) The pH values of a 1.0 mol dm^{-3} solution of $FeCl_3$ in water is given as y.

compound	pH of 1.0 mol dm^{-3} solution
$FeCl_3$	y

Table 5.1

With reference to the *Data Booklet*, quote relevant values and suggest whether the value of y is larger or smaller than 3. Explain your answer. [2]

(i) $AlCl_3$ dissolves to give $[Al(H_2O)_6]^{3+}$ which undergoes partial hydrolysis readily to form an acidic solution of pH 3.
Dissolving : $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
Marker writes BOD for $Al^{3+}(aq)$ for dissolving.
Hydrolysis : $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

[1]

(ii)

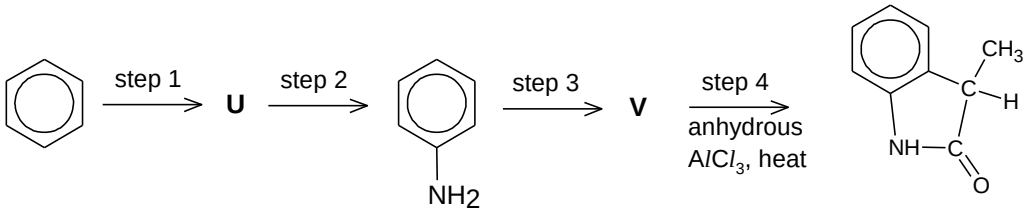
Ion	Size or radius of cation
Fe^{3+}	0.055
Al^{3+}	0.050

y >3 since Fe^{3+} has lower charge densityAl^{3+} , Fe^{3+} has a lower polarising power and lower degree/ extent of hydrolysis in aq solution, resulting in higher pH.

[2]

For Examiner's Use

(d) Compound **W** can be formed from benzene in the following reaction scheme.



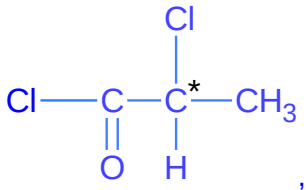
W

(i) Suggest the reagents and conditions for steps 1, 2 and 3.

(ii) Draw the structure of compound **V** in the space provided below. [1]

(iii) Draw the organic product obtained when compound **W** is treated with hot, acidified potassium manganate(VII). [1]

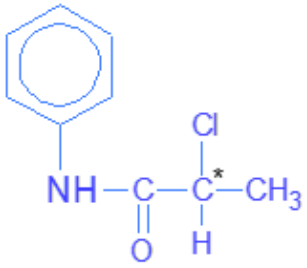
(i) Step 1: Concentrated H_2SO_4, concentrated HNO_3, 50°C/ 55°C
Step 2: 1.Sn, concentrated HCl, heat, followed by
2.NaOH(aq)



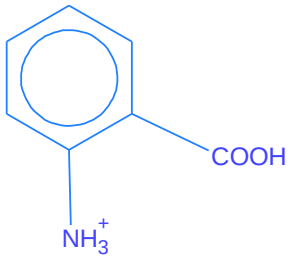
Step 3: , room temperature

[3]

(ii)



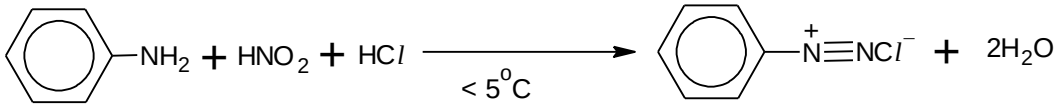
(iii)



(e) The following equations illustrate the formation of phenol from phenylamine, in two steps:

In step 1, phenylamine reacts with cold nitrous acid, HNO_2, and hydrochloric acid, HC*l*, to form phenyldiazonium chloride.

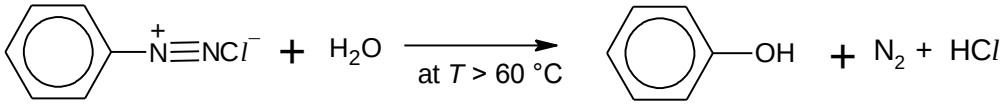
<u>step 1</u>



phenyldiazonium chloride

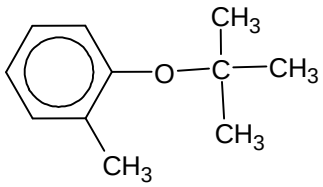
In step 2, phenyldiazonium chloride can react with water upon heating to give phenol.

<u>step 2</u>



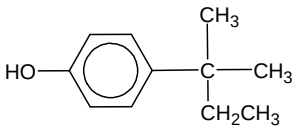
phenyldiazonium chloride

(i) By making use of the reactions above, propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



Compound S

(ii) Compound **T,** an isomer of Compound **S,** reacted with Br_2 in the presence of uv light to produce 3 different mono-brominated products, **X**, **Y** and **Z.**



Compound **T**

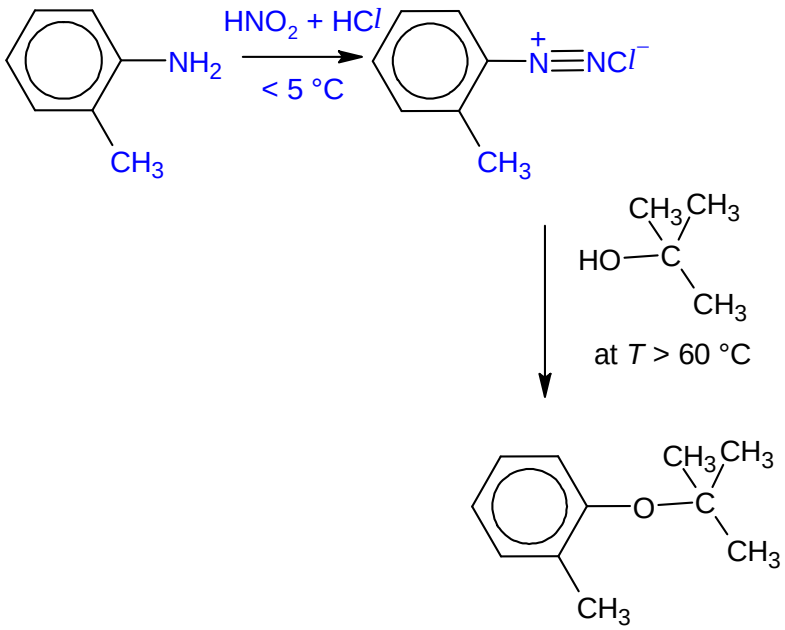
During free-radical substitution of alkanes, different types of hydrogen atoms are replaced by bromine atoms at different rates as shown in Table 5.2.

Table 5.2

Type of hydrogen atom	Reaction	Relative rate
Primary	$RCH_3 \rightarrow RCH_2Br$	1
Secondary	$R_2CH_2 \rightarrow R_2CHBr$	7
Tertiary	$R_3CH \rightarrow R_3CBr$	21

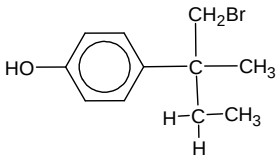
sing the information in Table 4.2 and considering the number and type of hydrogen atoms within the molecule **T**, draw the structures of the three monobrominated structural isomers formed and predict their relative ratio.

(i)

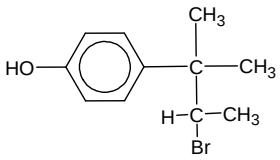


[2]

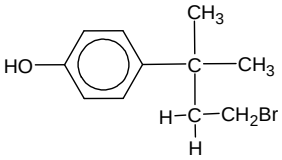
(ii)



6 x1
=6
=6



2x7
:14
:14



3x1
:3
:3

[3]

[Total:20]