Answer any **four** questions.

1 This question relates to the chemistry of Be, Mg, A*l* and their compounds.

(a) Beryllium compounds are toxic air pollutants. Inhalation of high levels of beryllium can cause inflammation of the lungs in humans and long-term exposure may cause chronic beryllium disease (*berylliosis*), in which granulomatous lesions develop in the lung.

(i) Given that charge density $\propto \frac{\text{ionic charge}}{\text{ionic radius}}$, calculate the relative charge densities of Be^{2+}, Mg^{2+} and Al^{3+}, using relevant data from the *Data* Booklet.

Be^{2+}: 64.5, Mg^{2+}: 30.8, Al^{3+}: 60.0

(ii) Hence, predict what is observed when aqueous sodium hydroxide is gradually added to aqueous beryllium sulfate until the sodium hydroxide is in an excess. Write equations for all reactions that have taken place.

- white ppt, which dissolves in excess NaOH to give a colourless solution

$Be^{2+}(aq) + 2OH^-(aq) \rightarrow Be(OH)_2(s)$

$Be(OH)_2(s) + 2OH^-(aq) \rightarrow Be(OH)_4^{2-}(aq)$

(iii) Suggest the pH of the solution formed when beryllium chloride is dissolved in water. Give your reasoning.

pH 3

Be^{2+} ions have high charge density, which polarises neighbouring H_2O molecules; hence, weakening O—H and H^+ lost

(iv) Magnesium ions are essential for the action of some enzymes (e.g. alkaline phosphatase found in the liver) by receiving electron pairs from oxygen and nitrogen atoms in the protein. It is thought that beryllium compounds are poisonous because they displace magnesium ions from these enzymes.

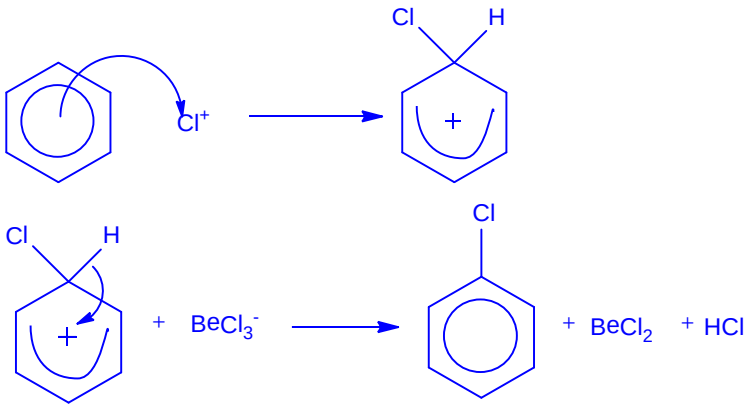
Suggest a reason why beryllium ions should behave in this way.

Be^{2+} ions have higher charge density (or greater polarising power) than Mg^{2+}; hence has greater tendency to receive electron pairs to form dative covalent bonds.

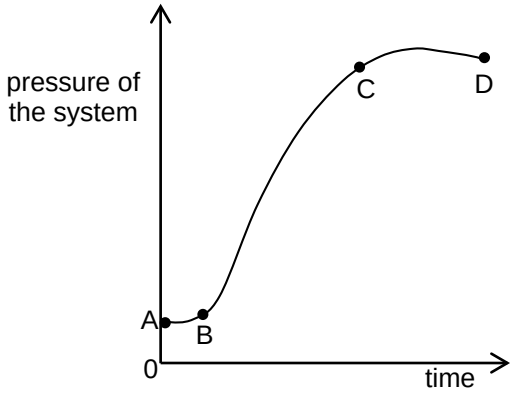
(v) Beryllium chloride may be used as a catalyst in the chlorination of benzene. Suggest a reason why this is possible. Outline the mechanism to show how beryllium chloride is involved in this reaction. [10]

In $BeCl_2$, Be atom has only 4 outer electrons and so, is able to act as lone pair acceptor (to generate Cl^+ electrophile)

$BeCl_2 + Cl_2 \rightarrow BeCl_3^- + Cl^+$



(b) A student carried out a kinetics experiment using a roll of magnesium ribbon that had been exposed to air for some time. He placed a piece of magnesium ribbon of mass 0.12 g into a flask containing 15.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid. The progress of the reaction was followed by measuring the pressure of the system at different times. The graph below shows the results of the experiment.



(i) Determine, by calculation, the limiting reagent for the experiment.

Mg + 2HC*l* ® MgC*l*$_2$ + H$_2$

amt of Mg = $\frac{0.12}{24.3}$ **= 0.00494 mol**

amt of HC*l* = 1.0 x $\frac{15.0}{1000}$ **= 0.015 mol**

since Mg º 2 HC*l*,

hence, amt of HC*l* required for reaction = 2 x 0.00494 = 0.00988 mol < 0.015 mol (initial amount of HC*l* used)

Hence, Mg is the limiting reagent.

(ii) Account for the change in pressure of the system as shown in the graph at points **A**, **B**, and from **C** onwards.

At A – initially rate is slow; due to layer of oxide/MgO formed on the surface of Mg ribbon due to oxidation in air

At B – rapid increase in rate; reaction is exothermic, heat evolved increases rate of reaction

C onwards – decrease in rate; as Mg (limiting reagent) is used up

[4]

(c) An alloy of aluminium and magnesium is used in boat-building.

A 1.75 g sample of the alloy was dissolved in the minimum volume of 4 mol dm^{-3} hydrochloric acid and the solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered and the residue, **X**, rinsed with distilled water, all washings being added to the filtrate, **Y**. After air drying, 0.18 g of **X** was obtained. Carbon dioxide was passed into **Y** and a white solid, **Z**, which contained aluminium, was collected. Heating **Z** to constant mass gave a residue of mass 3.16 g.

Suggest the identities of **X**, **Y** and **Z**, and determine the percentage composition by mass of the alloy.

On dissolution in HCl (aq):

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ (and) $Al + 3HCl \rightarrow AlCl_3(aq) + 3/2\ H_2(g)$

On addition of excess NaOH (aq) till no further reaction occurs:

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s)$ Residue X: $Mg(OH)_2$

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3(s)$
$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ Filtrate Y: $NaAl(OH)_4$ [not $Al(OH)_4^-$]

On addition of CO_2 into Y:

$2NaAl(OH)_4(aq) + CO_2 \rightarrow 2Al(OH)_3(s) + Na_2CO_3(aq)$ White solid Z: $Al(OH)_3$

Heating Z to constant mass:
$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(aq)$ residue of mass 3.16g = Al_2O_3 (s)

X – $Mg(OH)_2$

Y – $NaAl(OH)_4$

Z – $Al(OH)_3$

mass of Mg in $Mg(OH)_2$ = $\frac{24.3}{24.3+2(16.0+1.0)}$ x 0.18 = $\frac{24.3}{58.3}$ x 0.18 = 0.0750 g

mass of Al in Al_2O_3 = $\frac{2(27.0)}{2(27.0)+3(16.0)}$ x 3.16 = $\frac{54.0}{102.0}$ x 3.16 = 1.67 g

% of Mg in alloy = $\frac{0.0750}{1.75}$ x 100 = 4.29 %

% of Al in alloy = $\frac{1.67}{1.75}$ **x 100 = 94.4 %**

[6]

[Total: 20]

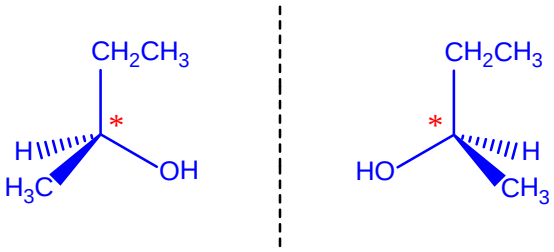
2 2-chlorobutane undergoes hydrolysis with NaOH(aq) via two different reaction pathways in the same reaction to form a mixture of two enantiomeric products.

$$CH_3CHClCH_2CH_3 + NaOH \rightarrow CH_3CH(OH)CH_2CH_3 + NaCl$$

In one of the hydrolysis reaction pathways, only one product is formed and inversion of configuration occurs in the product. For the other reaction pathway, a racemic mixture is formed.

(a) In an experiment, one optical isomer of 2-chlorobutane undergoes hydrolysis and two enantiomeric products in a ratio of 95%:5% are formed.

(i) Draw the structures of the two enantiomeric products.

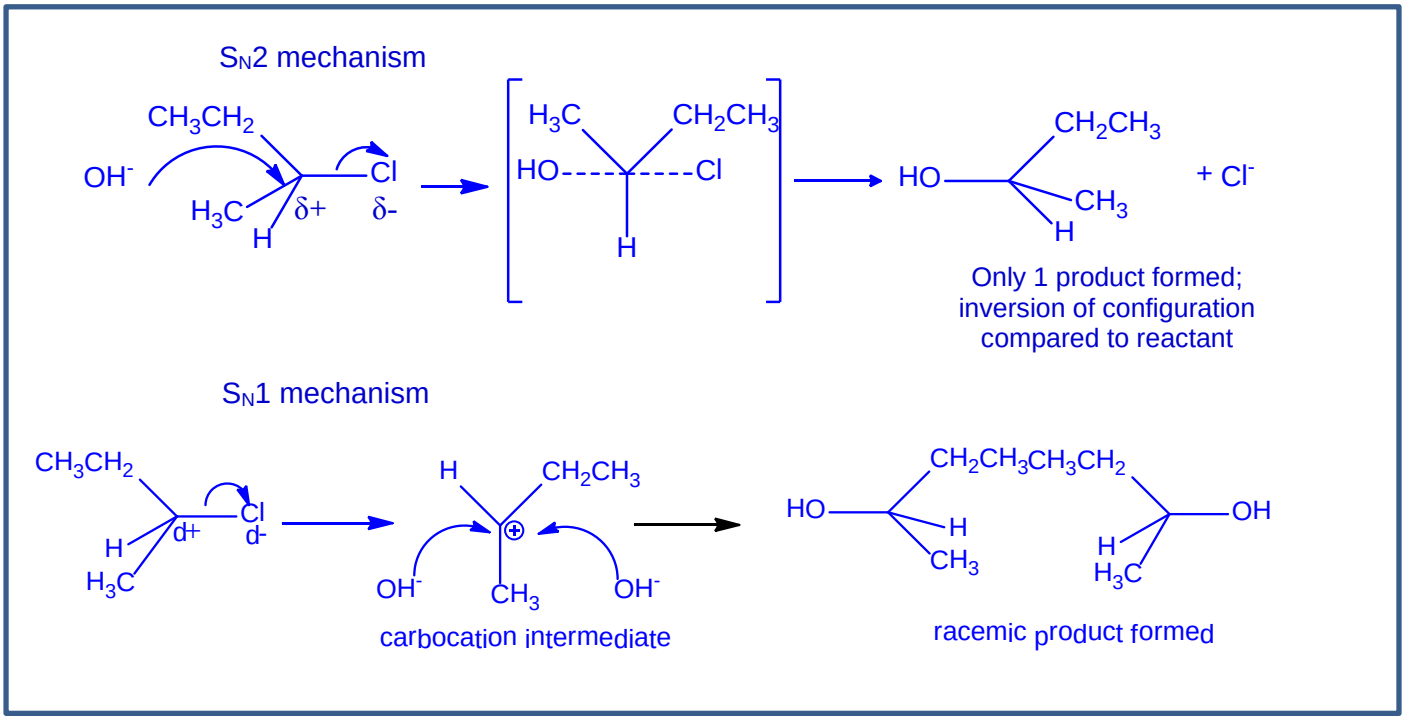


Few students scored full marks for this part. Many students could not represent the enantiomers appropriately.

Common errors:

1. ***No mirror line drawn (or) mirror line drawn as solid line.***
2. ***Enantiomers are not represented as mirror images of each other.***
3. ***Enantiomers are not represented in terms of tetrahedral geometry / 3D configuration.***
4. ***Wedge and dotted line of 3D configuration not drawn in correct direction.***
5. ***-CH_2CH_3 often wrongly represented as H_3CHC- in enantiomer structures.***

(ii) One enantiomer is formed in a much higher percentage compared to the other. Explain clearly how this disparity arises by examining the mechanisms of both reaction pathways. You should name both mechanisms involved but an outline of the mechanism is **not** required.

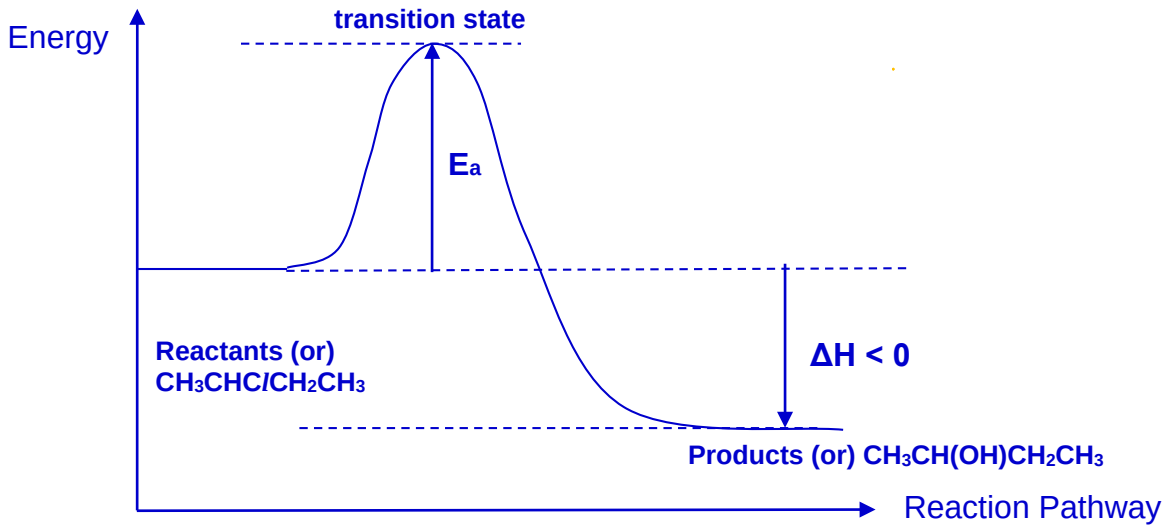


Hydrolysis of 2-chlorobutane **occurs via both S_N2 and S_N1 mechanisms**. **A racemic product is formed via the S_N1 mechanism** whereas only **1 chiral product is formed during the S_N2 mechanism**. As such, one of the enantiomers is formed in a greater proportion compared to the other.

One of the enantiomers is formed in **a much greater percentage as the reaction proceeds largely via the S_N2 mechanism** that results in the formation of 1 chiral product.

(iii) Write a rate equation for the reaction pathway that results in the inversion of the configuration and draw its energy profile diagram, given that the enthalpy change of the hydrolysis is exothermic.

rate = k[$CH_3CHClCH_2CH_3$][OH^-]



(iv) Suggest the percentage of 2-chlorobutane that undergoes hydrolysis via the reaction pathway in **(a)(iii)**.

90%

(v) Hence deduce how much faster the rate of this reaction pathway in **(b)(ii)** compares to that of the other reaction pathway.

9 times faster

[9]

(b) 2-chlorobutane is commonly produced from but-1-ene via reaction with hydrogen chloride.

$$CH_2{=}CHCH_2CH_3(g) + HCl(g) \rightarrow CH_3CHClCH_2CH_3(l)$$

(i) Name the other possible product in the above reaction.

1-chlorobutane

(ii) Predict the sign of ΔS for this reaction, showing your reasoning.

$CH_2{=}CHCH_2CH_3$ (g) + HCl (g) à $CH_3CHClCH_2CH_3$ (l)

$\Delta S < 0$

Since 1 mol of $CH_3CHClCH_2CH_3$ (*l*) is formed from 1 mol of $CH_2{=}CHCH_2CH_3$ (g) and 1 mol of HCl (g), **number of gas molecules in the system decreases as reaction proceeds**. As molecules in the gaseous state have more ordered arrangement, hence **entropy of system decreases**.

(iii) Using relevant bond energy values from the *Data Booklet*, calculate the approximate value of ΔH for the reaction in **(b)**.

$CH_2{=}CHCH_2CH_3$ (g) + HCl (g) à $CH_3CHClCH_2CH_3$ (l)

Bond broken	Bond Energy / kJ mol^{-1}	Bond formed	Bond energy / kJ mol^{-1}
C=C	+610	C-C	-350
H-Cl	+431	C-H	-410
		C-Cl	-340

ΔH = +610 + 431 -350 -410 – 340 = -59 kJ mol^{-1}

(iv) Bond energies quoted from the *Data Booklet* are average values. Other than this, explain why the method in **(b)(iii)** is not the most accurate for determining ΔH of the reaction.

$CH_3CHClCH_2CH_3$ formed in the reaction is a liquid, whereas the bond energy method is only applicable for a gaseous system / bond energy refers to the energy required to break 1 mole of a covalent bond between two atoms in the gaseous state whereas $CH_3CHClCH_2CH_3$ formed is in the liquid state.

(v) Deduce how the rate of reaction of but-1-ene with hydrogen halides will vary from H-F to H-I, and give your reasoning.

The rate of reaction will increase from H-F to H-I as the bond energy of H-X decreases from H-F to H-I.

As the rate determining step of the mechanism involves the breaking of the H-X bond, the weaker the H-X bond, the more readily it will break, thus increasing the rate of reaction with but-1-ene.

This question was generally well-answered.

(vi) While HC*l* react readily with alkenes under room conditions, HCN does not. Based on concepts of chemical bonding, suggest possible reasons for this.

HCN is a weaker electrophile than HC*l*.
C-H bond in HCN is non-polar in nature, hence C-H bond does not break readily to release H^+.

[10]

(c) HC*l* can be prepared by adding concentrated sulphuric acid to solid sodium chloride. However when concentrated sulphuric acid is added to sodium iodide, the yield of HI is very low. Explain. [1]

I^- is a stronger reducing agent compared to Cl^- hence it is able to further react with H_2SO_4 by reducing it to H_2S while itself is oxidised to I_2. As such, small amount of HI remains.

[Total: 20]

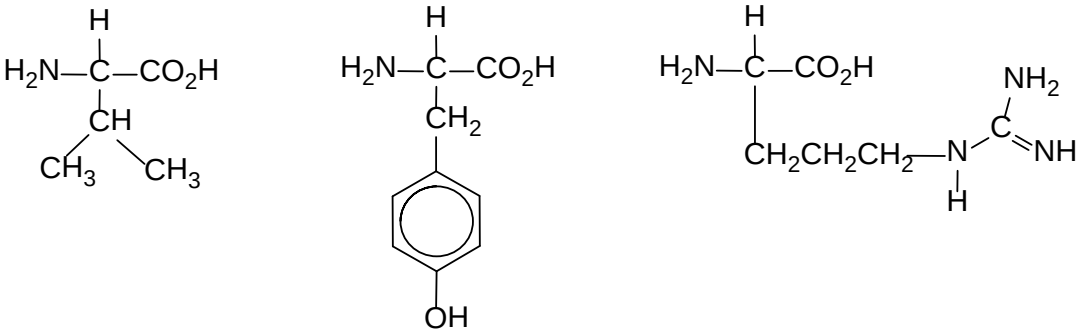
3 This question explores the chemistry of zinc in biochemistry, organic chemistry and electrochemistry.

(a) Angiotensin I, a simple protein, undergoes hydrolysis with the aid of an enzyme, known as angiotensin-converting enzyme (ACE) to form angiotensin II. Angiotensin II is an important hormone that causes blood vessels to constrict, resulting in a rise in blood pressure.

(i) State how proteins can be hydrolysed to form a mixture of their constituent amino acids.

6 mol dm^{-3} HC*l* or H_2SO_4 or NaOH, and heat for several hours (eg 6 hours)

Some of the amino acids found in angiotensin II are shown below.



valine (val) | tyrosine (tyr) | arginine (arg)

The side chains (R-groups) of angiotensin II could bind to targeted proteins through suitable R-group interactions. The R-group interactions are also used to maintain two specific protein structures.

(ii) Briefly describe **one** protein structure that involves R-group interactions.

Tertiary structure and its description (also accept quaternary structure)

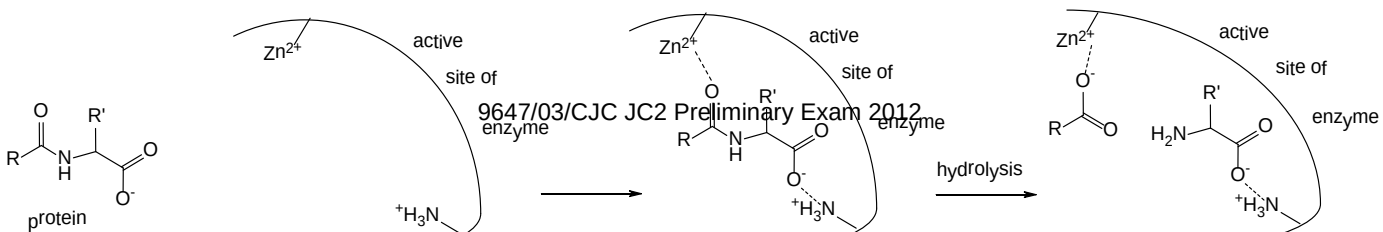
(iii) Suggest **three** different types of R-group interactions in which the side chains of angiotensin II could bind to targeted proteins. Your answer should clearly indicate the side chains that might be involved.

van der waals' forces of attraction with $-CH(CH_3)_2$ from valine or $-CH_2-C_6H_5$ from tyrosine or $-CH_2CH_2CH_2-$ from arginine (or non-polar alkyl side chain)

hydrogen bonding with phenol from tyrosine or –C=NH or $-NH_2$ from arginine

ionic bonding with $-NH_3^+$ group from arginine

(iv) Another enzyme that functions similarly as ACE is carboxypeptidase. The active site of carboxypeptidase contains $-NH_3^+$ group and a Zn^{2+} ion, which are both crucial in binding to suitable proteins. Below shows the hydrolysis of a protein (represented by $RCONHCH(R')CO_2^-$) catalysed by this enzyme.



If there is a mutation such that carboxypeptidase does not contain Zn^{2+}, it will fail to function effectively as a catalyst. By using the above information, suggest why.

Protein cannot effectively bind to active site of enzyme due to absence of ion-dipole attractions between Zn^{2+} ions and C=O group

[6]

(b) Lucas reagent is used to distinguish primary, secondary and tertiary alcohols. It consists of a solution of anhydrous $ZnCl_2$ in concentrated HCl. Upon addition of Lucas' reagent at 28 °C, tertiary alcohols give immediate cloudiness, secondary alcohols give cloudiness within 5 minutes and primary alcohols have no cloudiness. The overall reaction that has occurred can be represented as

$$ROH + HCl \text{ à } RCl + H_2O$$

(i) Draw **three** structural isomers with molecular formula $C_4H_{10}O$ that can be distinguished using Lucas reagent and state the observation for each isomer.

$CH_3CH_2CH_2CH_2OH$ or $(CH_3)_2CHCH_2OH$: no cloudiness
$CH_3CH(OH)CH_2CH_3$: cloudiness within 5 minutes
$(CH_3)_3COH$: immediate cloudiness

(ii) Hence from your observation in part **(i)**, suggest a possible product that is responsible for the cloudiness of the mixture.

$CH_3CH(Cl)CH_2CH_3$ or $(CH_3)_3CCl$

(iii) Four structural isomers of molecular formula $C_3H_6O_2$ are:

- **E**: $CH_3CH(OH)CHO$
- **F**: CH_3COCH_2OH
- **G**: $HOCH_2CH_2CHO$
- **H**: $HCO_2CH_2CH_3$

Show how isomers **E** to **H** can be adequately distinguished from one another by the use of simple chemical tests. You should also give brief descriptions of the chemical tests and expected observations for each isomer.

		E: $CH_3CH(OH)CHO$	F: CH_3COCH_2OH	G: $HOCH_2CH_2CHO$	H: $HCO_2CH_2CH_3$
1	Add Lucas' reagent.	Cloudiness within 5 minutes	No cloudiness	No cloudiness	No cloudiness
2	Add Na metal.	Effervescence (of H_2) observed	Effervescence (of H_2) observed	Effervescence (of H_2) observed	No Effervescence
3	Add $SOCl_2$ or PCl_5.	Steamy fumes (of HCl) observed	Steamy fumes (of HCl) observed	Steamy fumes (of HCl) observed	No fumes
4	Add alkaline I_2(aq) and heat.	Yellow ppt (of CHI_3) formed.	Yellow ppt (of CHI_3) formed.	No ppt	Yellow ppt (of CHI_3) formed. (due to CH_3CH_2OH formed on hydrolysis.)
5	Add 2,4-dinitrophenyl-hydrazine and heat.	Orange ppt formed	Orange ppt formed	Orange ppt formed	No ppt
6	Add Tollens' reagent and heat.	Silver mirror formed	No silver mirror	Silver mirror formed	No silver mirror
7	Add Fehling's solution and heat.	Red ppt (of Cu_2O) formed	No ppt	Red ppt (of Cu_2O) formed	No ppt
8	Add acidified $KMnO_4$ and heat.	Purple $KMnO_4$ decolourised.	Purple $KMnO_4$ decolourised.	Purple $KMnO_4$ decolourised.	Purple $KMnO_4$ decolourised and effervescence (of CO_2) observed. [due to formation of HCO_2H on acidic hydrolysis, which gets oxidised to CO_2 and H_2O.

[7]

(c) About 12 million tonnes of zinc are produced every year, of which 70 % are obtained through mining. The ore is first roasted to produce zinc oxide, which is then further processed to obtain pure zinc through a series of steps.

(i) In the first step, ZnO is reacted with dilute sulfuric acid. Write a balanced equation for this reaction.

$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$ or $ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$

The next step involves electrolysis of the resulting solution obtained in **(i).** A current of 10 000 A is passed through the solution in a series of electrolytic cells and zinc is deposited on the cathode of each cell. After 24 hours, each cell is shut down, the zinc coated cathodes are rinsed and pure zinc is mechanically stripped from the cathode.

(ii) Write the half-equations for each electrode reaction and hence, construct the overall balanced equation.

At cathode: $Zn^{2+} + 2e \rightarrow Zn$

At anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e$

Overall: $2Zn^{2+} + 2H_2O \rightarrow 2Zn + O_2 + 4H^+$

(iii) Assuming that only one cell is involved in the production in a 24-hour period

I Calculate the mass of zinc produced in 24 hours.

$Zn^{2+} \equiv 2e \equiv Zn$

Total charge passed through in 24 hours = 10 000 x 24 x 60 x 60

$= 8.64 \times 10^8$ C

Amount of electrons = $\frac{8.64 \times 10^8}{9.65 \times 10^4}$ = 8.953×10^3 mol

Amount of Zn = $\frac{1}{2}$ x 8.953×10^3 = 4.477×10^3 mol

Mass of Zn = $4.477 \times 10^3 \times 65.4 = 2.93 \times 10^5$ g (= 293 kg)

II Hence, calculate the thickness, in cm, of the zinc sheet produced.

Given: current density = 500 A m^{-2} of zinc deposited

density of zinc = 7.14 g cm^{-3}.

[Current density is defined as the current flowing per unit area]

Total volume of Zn deposited = $\frac{2.93 \times 10^5}{7.14}$ = 4.1036×10^4 cm^3

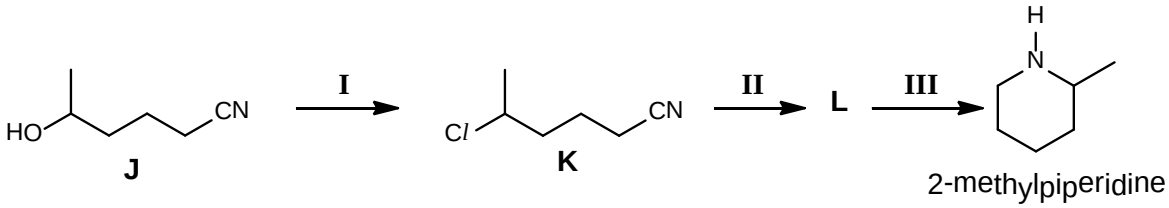
Total surface area = $\frac{10\,000}{500}$ = 20 m^2 = 2×10^5 cm^2

Thickness = $\frac{4.1036 \times 10^4}{2.00 \times 10^5}$ = 0.205 cm

[7]

[Total: 20]

4 Piperidines are widely used building blocks in the synthesis of organic compounds in the pharmaceutical industry. A possible synthetic route of 2-methylpiperidine is shown below.



(a) (i) State the type of reaction that has occurred in stage **I** and identify a suitable reagent used.

Nucleophilic substitution

PCl_5 / PCl_3 / $SOCl_2$

(ii) Explain why stage **I** has to be carried out in an anhydrous condition. Include in your answer any relevant equation.

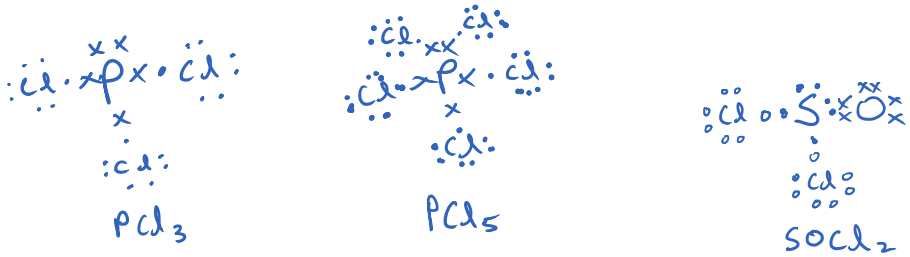
PCl_5 / PCl_3 / $SOCl_2$ undergoes hydrolysis when reacted with water.

$PCl_5 + H_2O \rightarrow POCl_3 + 2\,HCl$

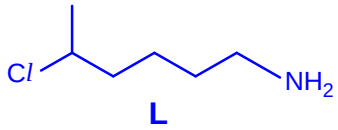
OR $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

OR $SOCl_2 + H_2O \rightarrow SO_2 + 3HCl$

(iii) Draw the dot-and-cross diagram of the reagent used in stage **I.**



(iv) Suggest the structure of compound **L** and state the reagent and conditions required in stage **II**.



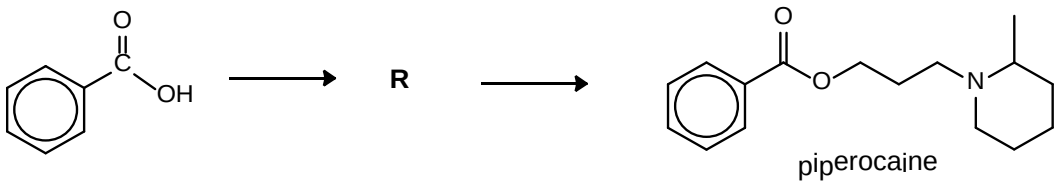
L

LiA*l*H$_4$ in dry ether, r.t.p.

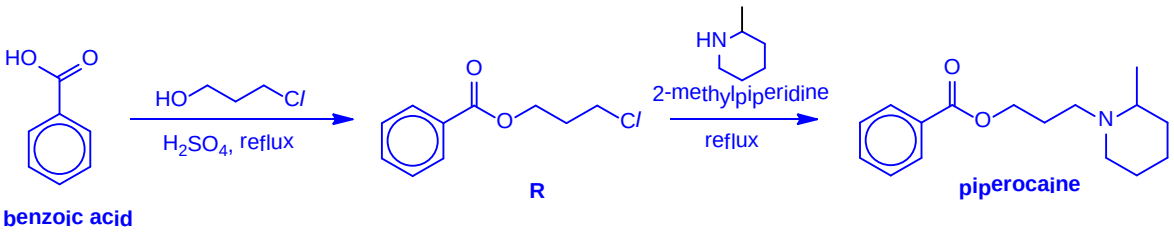
OR heat with H$_2$ over Ni catalyst at 140^{o}C

[8]

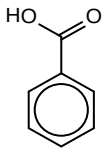
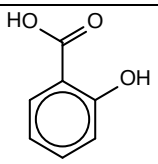
(b) Benzoic acid and 2-methylpiperidine can be used to synthesise piperocaine (shown below), a local anaesthesia used for infiltration and nerve block, via a two-step reaction. Benzoic acid is first converted into an intermediate, **R**, which is then converted to piperocaine.



Suggest a synthetic route for piperocaine. State clearly the reagents and conditions required for each step and draw the structure of intermediate **R** produced. [4]



(c) Benzoic acid is used as an antiseptic due to its ability to inhibit the growth of bacteria. Salicylic acid, a monohydroxybenzoic acid, has a similar function. The structure and solubility of both compounds in water are shown in the table below.

Name	Structure	Solubility / mol dm^{-3}
Benzoic acid		0.0238
Salicylic acid		0.0145

(i) By considering structure and bonding, explain the difference in solubility of benzoic acid and salicylic acid.

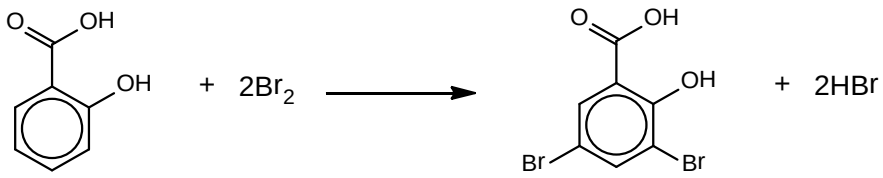
Both compounds are simple covalent molecules and can form hydrogen bonding with water molecules.

However, intramolecular hydrogen bonding is present in salicylic acid due to the close proximity of the carboxyl group and hydroxyl group.

Thus, the hydrogen bonding between salicylic acid and water is less extensive than the hydrogen bonding between benzoic acid and water.
This results in the lower solubility of salicylic acid in water.

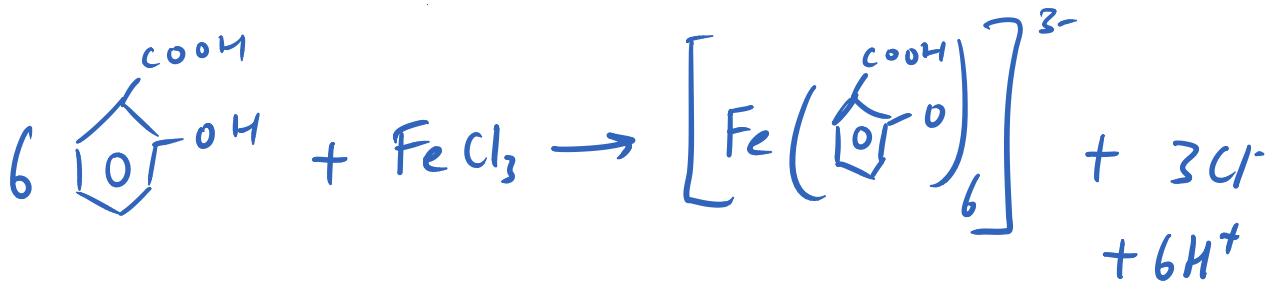
(ii) Suggest a simple chemical test that can be used to distinguish benzoic acid from salicylic acid. State the reagents and conditions used and describe clearly the observations for each of the compound. Write a balanced equation for any reaction that occurs.

Add **Br_2(aq)** to each compound separately at **room temperature**.
Br_2(aq) turned from **brown to colourless** when reacted with salicylic acid due to the presence of phenol.
Br_2(aq) **remained brown** when reacted with benzoic acid



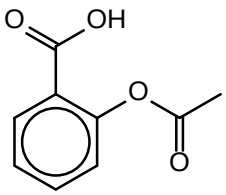
OR

Add **Neutral $FeCl_3$(aq)** to each compound separately
Purple Coloration when reacted with salicylic acid due to the presence of phenol.
No such coloration with benzoic acid



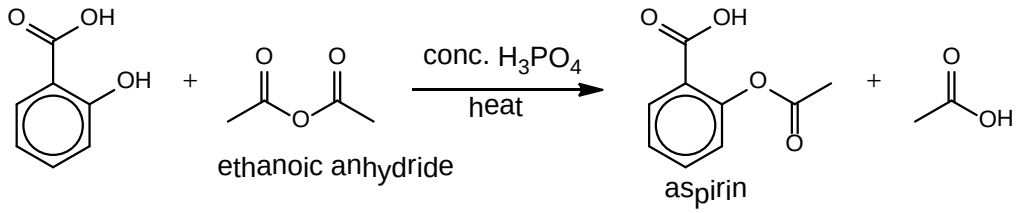
[5]

(d) Salicylic acid is also an important active metabolite of aspirin(shown below), a drug to relieve minor aches and pains, to reduce fever, and as an anti-inflammatory medication.



aspirin

The synthesis of aspirin involves treating salicylic acid with ethanoic anhydride, an acid derivative, in the presence of concentrated phosphoric acid. This esterification process (shown below) yields aspirin and ethanoic acid, which is considered a by-product of this reaction.

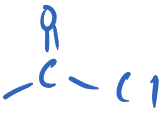


(i) Suggest why salicylic acid will not react with itself to produce an ester given the conditions stated above.

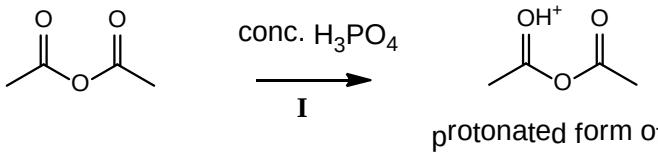
Phenol is too weak a nucleophile (*as the lone pair of electrons on the oxygen can delocalised into the benzene ring, thus less available for donation)* for esterification with benzoic acid to occur.

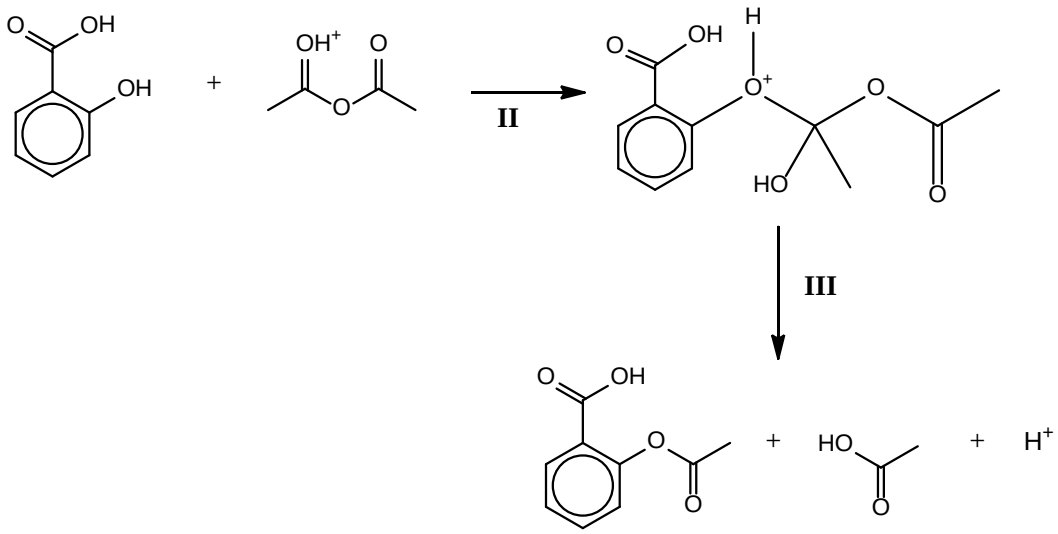
(ii) Suggest another reagent that can be used in place of ethanoic anhydride in the synthesis of aspirin from salicyclic acid.

Ethanoyl Chloride



(iii) The synthesis of aspirin from salicyclic acid with ethanoic anhydride may oocur as follows.





Suggest the types of reactions occurring in stage **I** and **II**.

I. **Acid-base reaction**

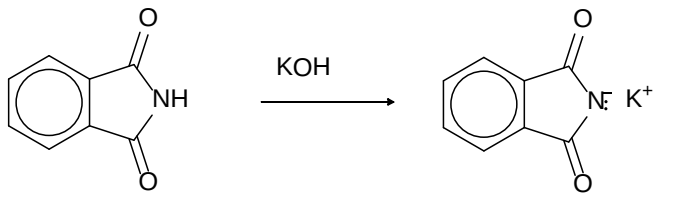
II. **Nucleophilic addition**

[3]

[Total: 20]

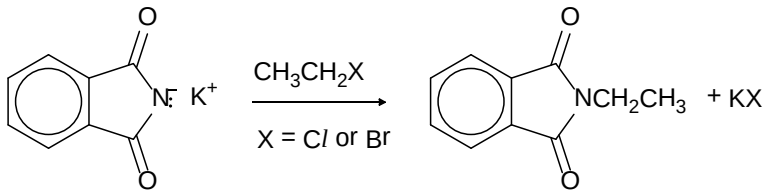
5 **(a)** The Gabriel synthesis is a chemical reaction that transforms primary alkyl halides into primary amines using potassium phthalimide. It gives a high yield of primary amines and an example of the Gabriel synthesis is shown below.

Step **I**

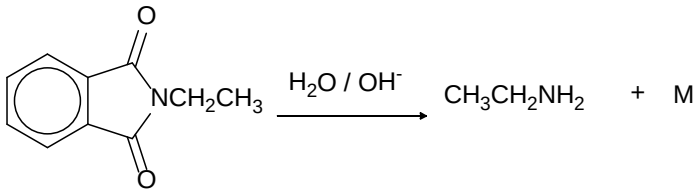


potassium phthalimide

Step **II**



Step **III**



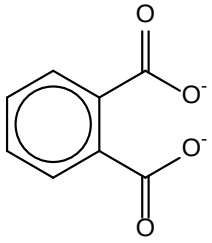
(i) Step **I** is unusual as the amide hydrogen is quite acidic, hence it can react with KOH to produce potassium phthalimide. Suggest why the amide hydrogen is acidic in this case.

Presence of two electron-withdrawing C=O groups increases polarisation of N-H bond and weakens the N-H bond, hence amide hydrogen is acidic.

(ii) What *type* of reaction is step **III**?

Step II: hydrolysis

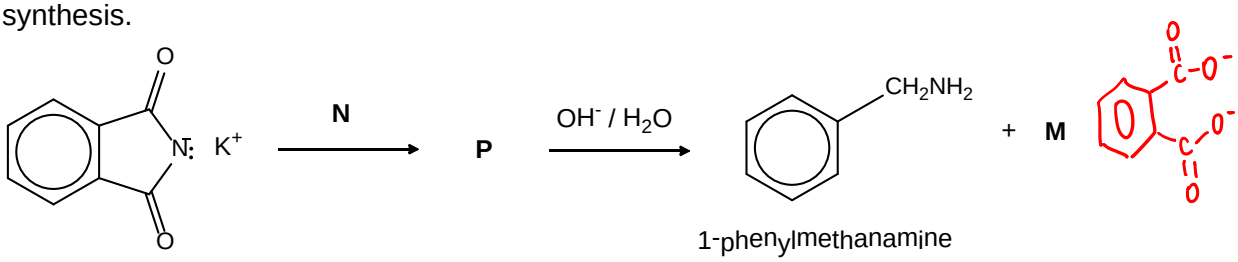
(iii) Suggest a structure for **M**.



[3]

(b) 1-phenylmethanamine ($C_6H_5CH_2NH_2$) is a versatile organic compound which is used as a raw material for the production of Vitamin H and is also an active ingredient in the production of nylon fibres.

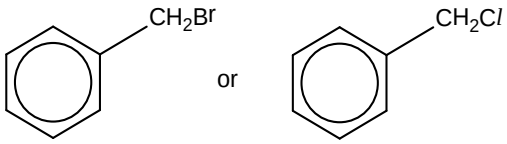
1-phenylmethanamine can be produced via a similar two-step Gabriel amine synthesis.



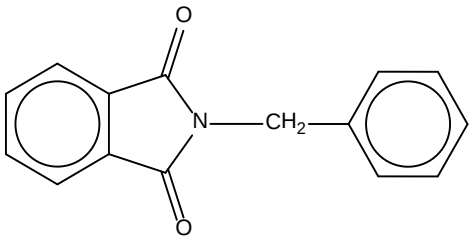
1-phenylmethanamine

Suggest the structures of compounds **N** and **P**. [2]

N:

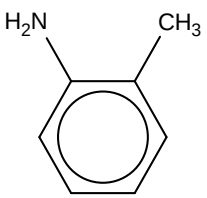


P:

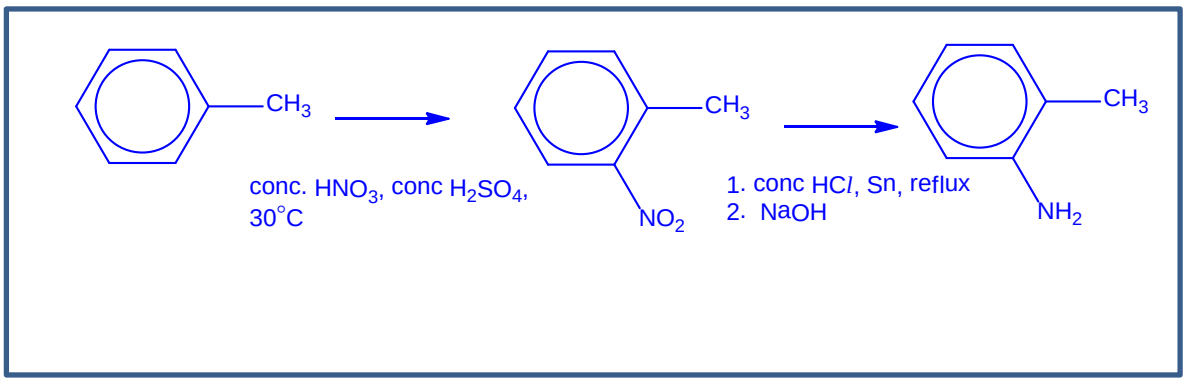


(c) Phenylamine, along with its chlorine-substituted derivatives, is widely used in biology, medicine as well as the paint and varnish industry.

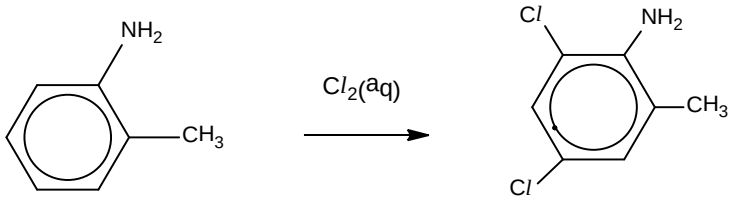
(i) Suggest a synthetic route to form 2-methylphenylamine from methylbenzene.



2-methylphenylamine



(ii) The reaction below can proceed in the absence of a catalyst. Explain why milder conditions are required for this reaction compared to chlorination of benzene.



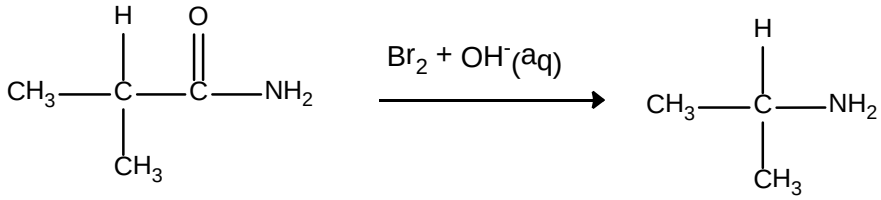
Presence of electron-donating NH_2 group increases electron-density on the benzene ring or activates the ring towards electrophilic substitution and thus milder conditions are required for the reaction to occur. Aqueous chlorine is used to allow polysubstitution to occur.

Comments

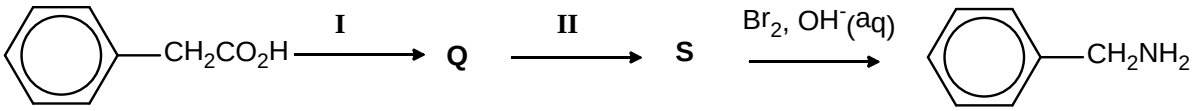
(1) Many students lose this mark due to poor phrasing, using words like "charge density of the benzene" or "the negativity of the benzene ring" is increased. These are not accepted since it is not an ion to begin with!

[3]

(d) The Hofmann rearrangement is another organic reaction used to synthesis primary amines. It involves the reaction of a primary amide with aqueous alkaline bromine to form a primary amine with one less carbon atom than the starting material.

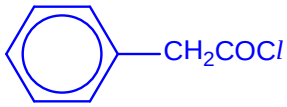


1-phenylmethanamine ($C_6H_5CH_2NH_2$) can also be produced in a three-step sequence given below where the last step is a Hofmann reaction.

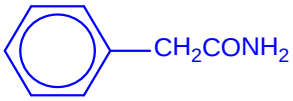


(i) Draw the structures of compounds **Q** and **S**.

Q:



S:



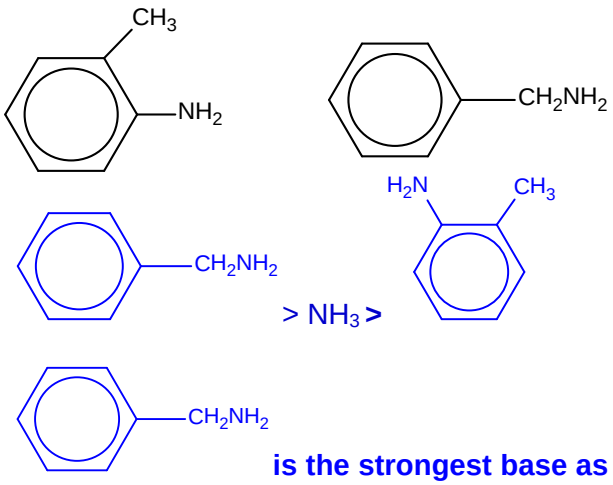
(ii) Suggest reagents and conditions required for stages **I** and **II**.

Stage I:PCl_5, rt / SOCl_2, reflux / PCl_3 reflux

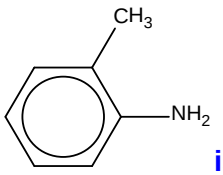
Stage II: NH_3, rt

[4]

(e) (i) Arrange the following compounds in order of decreasing basicity. Explain your answer.



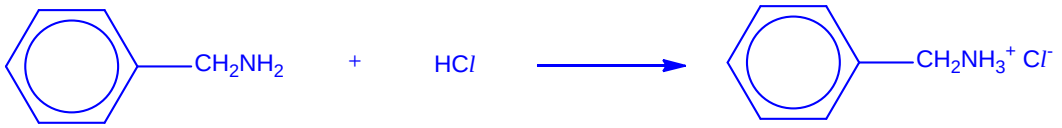
is the strongest base as the presence of electron-donating alkyl group increases availability of lone pairs of electrons on N and thus make it more available to accept a proton.



is the weakest base as the lone pair of electrons on N can be delocalised into the benzene ring and thus lone pair of electrons is less available to accept proton.

(ii) Calculate the pH of the resulting solution when 25 cm^3 of 0.0200 mol dm^{-3} HCl is added to 25 cm^3 of 0.0300 mol dm^{-3} 1-phenylmethanamine ($C_6H_5CH_2NH_2$).

(The K_b value of 1-phenylmethanamine is 2.19 x 10^{-5} mol dm^{-3}.)



25 × $\frac{0.03}{1000}$ = 0.00075 mol **25 × $\frac{0.02}{1000}$ = 0.0005 mol** **= 0.0005 mol**

A weak base and the conjugate acid is present in the final solution (i.e. alkaline buffer present)

pOH = pKb + lg $\frac{[salt]}{[base]}$ = - lg (2.19 x 10^{-5}) + lg $\frac{0.0005}{0.00025}$ = 4.961

pH = 14 - 4.961 = 9.04

(iii) A 0.0200 mol dm^{-3} solution of 1-phenylmethanamine was mixed with an equal volume of 0.00100 mol dm^{-3} of aqueous magnesium sulfate. Determine whether a precipitate would be formed in this experiment.

(The numerical K_{sp} value of magnesium hydroxide is 1.8 x 10^{-12}).

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$[OH^-] = \sqrt{2.19 \times 10^{-5} \times 0.01}$ = 0.0004680 mol dm^{-3}

Ionic product of $Mg(OH)_2$ = $[Mg^{2+}][OH^-]^2$ = $\frac{0.001}{2}$ x $(0.0004680)^2$
= 1.10 x 10^{-10} > Ksp of $Mg(OH)_2$

Yes, a precipitate would be formed.

[8]

[Total: 20]