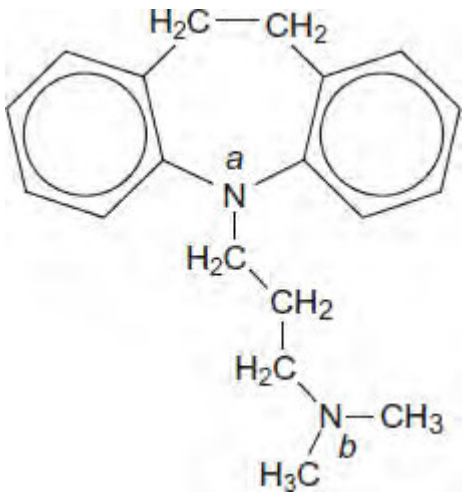
Q1. Imipramine has been prescribed as an antidepressant. The structure of imipramine is shown below.



(a) The medicine is usually supplied as a salt. The salt is formed when one mole of imipramine reacts with one mole of hydrochloric acid.

Suggest why the nitrogen atom labelled *b* is more likely to be protonated than the nitrogen atom labelled *a* when the salt is formed.

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(3)

(b) Deduce the molecular formula of imipramine and give the number of peaks in its ^{13}C n.m.r. spectrum.

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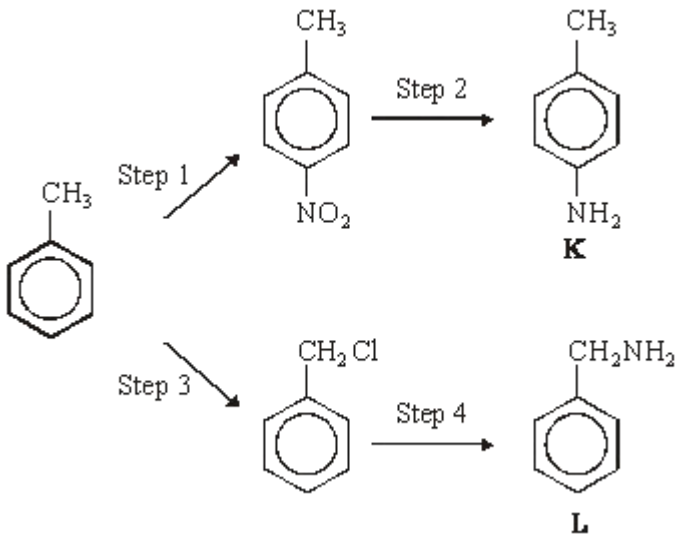
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(2)
(Total 5 marks)

Q2. The following reaction scheme shows the formation of two amines, **K** and **L**, from methylbenzene.



(a) (i) Give the reagents needed to carry out Step 1. Write an equation for the formation from these reagents of the inorganic species which reacts with methylbenzene.

Reagents .....

Equation .....

(ii) Name and outline a mechanism for the reaction between this inorganic species and methylbenzene.

Name of mechanism .....

Mechanism

(7)

(b) Give a suitable reagent or combination of reagents for Step 2.

.....

(1)

(c) (i) Give the reagent for Step 4 and state a condition to ensure that the primary amine is the major product.

Reagent .....

Condition .....

(ii) Name and outline a mechanism for Step 4.

Name of mechanism .....

Mechanism

(7)
(Total 15 marks)

Q3. Which one of the following reactions does **not** involve donation of an electron pair?

A $H^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$

B $AlCl_3 + Cl^- \rightarrow A1C1_4^-$

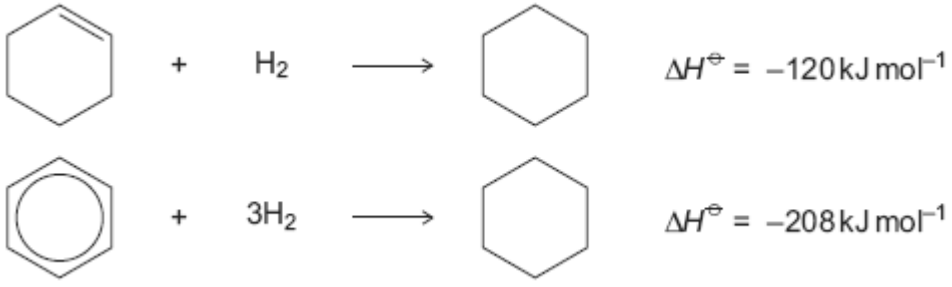
C $CH_3Cl + CN^- \rightarrow CH_3CN + Cl^-$

D $\frac{1}{2}Cl_2 + I^- \rightarrow Cl^- + \frac{1}{2}I_2$

(Total 1 mark)

Q4. The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

(a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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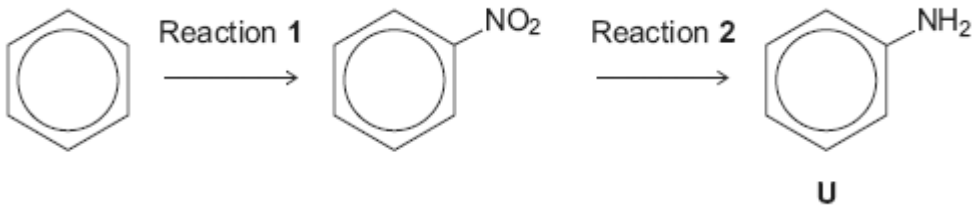
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(4)

(b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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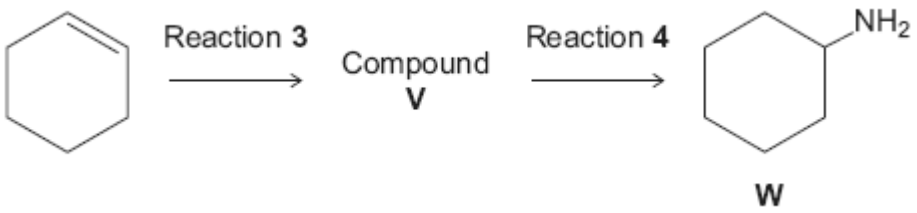
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(6)

(c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(Extra space) .....

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(6)

(d) Explain why amine **U** is a weaker base than amine **W**.

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(Extra space) .....

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(3)
(Total 19 marks)

Q1. (a) Name and outline a mechanism for the formation of butylamine, $CH_3CH_2CH_2CH_2NH_2$, by the reaction of ammonia with 1-bromobutane, $CH_3CH_2CH_2CH_2Br$.

Name of mechanism .....

Mechanism

(5)

(b) Butylamine can also be prepared in a two-step synthesis starting from 1-bromopropane, $CH_3CH_2CH_2Br$. Write an equation for each of the two steps in this synthesis.

Step 1

.....

Step 2

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(3)

(c) (i) Explain why butylamine is a stronger base than ammonia.

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(ii) Identify a substance that could be added to aqueous butylamine to produce a basic buffer solution.

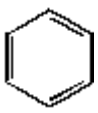
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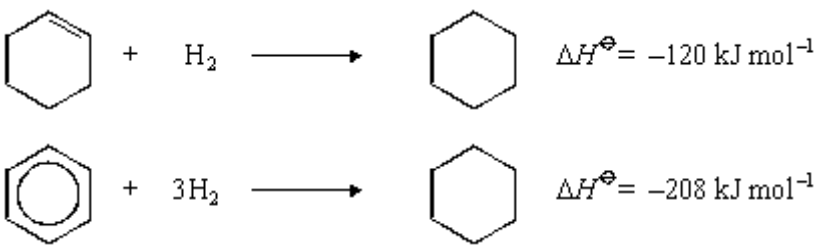
(d) Draw the structure of a tertiary amine which is an isomer of butylamine.

(1)
(Total 12 marks)

Q2. (a) Use the following data to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.

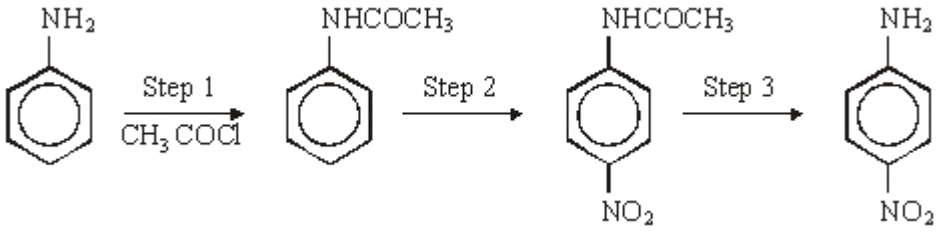


Give a reason for this difference in stability.



(4)

(b) Consider the following reaction sequence which starts from phenylamine.



(i) State and explain the difference in base strength between phenylamine and ammonia.

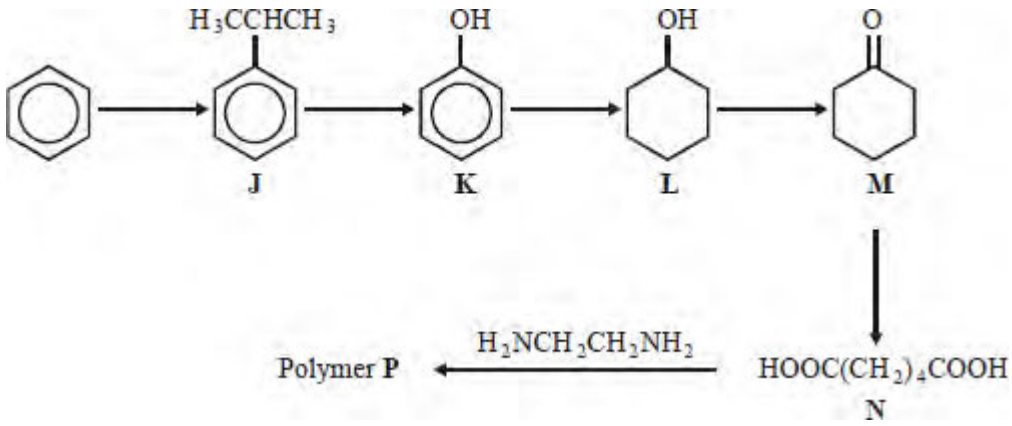
(ii) Name and outline a mechanism for the reaction in Step 1 and name the organic product of Step 1.

(iii) The mechanism of Step 2 involves attack by an electrophile. Give the reagents used in this step and write an equation showing the formation of the electrophile.
Outline a mechanism for the reaction of this electrophile with benzene.

(iv) Name the type of linkage which is broken in Step 3 and suggest a suitable reagent for this reaction.

(17)
(Total 21 marks)

Q3. This question is about the following reaction scheme which shows the preparation of polymer **P**.



Polymer **P** is formed in a two-step reaction from **N**. The first stage is a neutralisation reaction. The volume, in cm^3, of a 0.20 mol dm^{-3} solution of $H_2NCH_2CH_2NH_2$ required to neutralise 6.8×10^{-3}mol of the acid **N** is

A 17

B 34

C 68

D 136

(Total 1 mark)

Q4. (a) Methylamine is a weak Brønsted-Lowry base and can be used in aqueous solution with one other substance to prepare a basic buffer.

(i) Explain the term *Brønsted-Lowry base* and write an equation for the reaction of methylamine with water to produce an alkaline solution.

Brønsted-Lowry base .....

Equation .....

(ii) Suggest a substance that could be added to aqueous methylamine to produce a basic buffer.

.....

(iii) Explain how the buffer solution in part (a)(ii) is able to resist a change in pH when a small amount of sodium hydroxide is added.

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(5)

(b) Explain why methylamine is a stronger base than ammonia.

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(2)

(c) A cation is formed when methylamine reacts with a large excess of bromoethane. Name the mechanism involved in the reaction and draw the structure of the cation

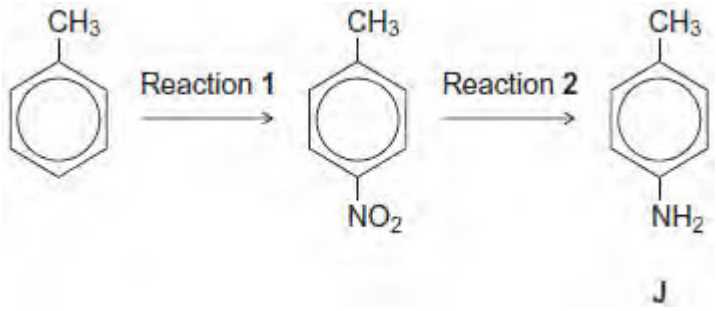
formed.

Name of mechanism .....

Structure

(2)
(Total 9 marks)

Q1. Consider the following reaction sequence starting from methylbenzene.



(a) Name the type of mechanism for reaction **1**.

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(1)

(b) Compound **J** is formed by reduction in reaction **2**.

(i) Give a reducing agent for this reaction.

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(1)

(ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

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(1)

(iii) Give a use for **J**.

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(1)

(c) Outline a mechanism for the reaction of bromomethane with an excess of compound **J**.
You should represent **J** as RNH_2 in the mechanism.

(4)

(d) Compound **K** ($C_6H_5CH_2NH_2$) is a structural isomer of **J**.

Explain why **J** is a weaker base than **K**.

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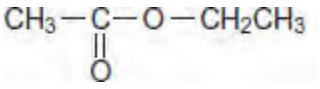
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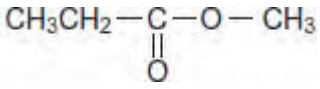
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(3)
(Total 11 marks)

Q2.(a) **Ester 1** and **Ester 2** were studied by ^{1}H n.m.r. spectroscopy.

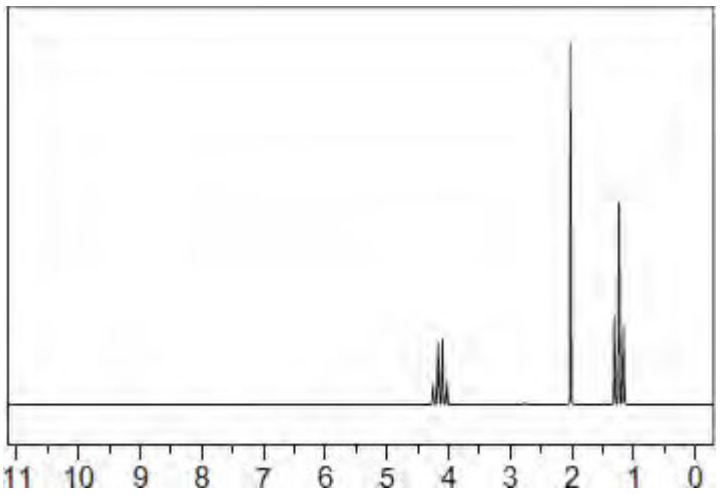


Ester 1



Ester 2

One of the two esters produced this spectrum.



Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at δ = 4.1 ppm in the spectrum.

Predict the δ value of the quartet peak in the spectrum of the other ester.

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

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(4)

(b) Cetrimide is used as an antiseptic.

$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-$

cetrimide

Name this type of compound.

Give the reagent that must be added to $CH_3(CH_2)15NH_2$ to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

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(4)

(c) Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.
Describe what you would see when the reagent is added to each compound and the test tube is shaken.

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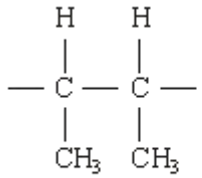
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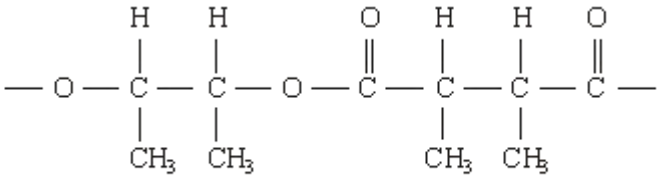
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(3)
(Total 11 marks)

Q3. (a) The repeating units of two polymers, **P** and **Q**, are shown below.



P



Q

(i) Draw the structure of the monomer used to form polymer **P**. Name the type of polymerisation involved.

Structure of monomer

Type of polymerisation .....

(ii) Draw the structures of **two** compounds which react together to form polymer **Q**. Name these **two** compounds and name the type of polymerisation involved.

Structure of compound 1

Name of compound 1 .....

Structure of compound 2

Name of compound 2 .....

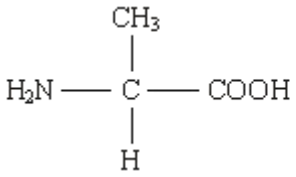
Type of polymerisation .....

(iii) Identify a compound which, in aqueous solution, will break down polymer **Q** but not polymer **P**.

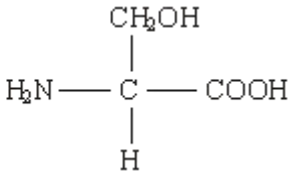
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(8)

(b) Draw the structures of the **two** dipeptides which can form when one of the amino acids shown below reacts with the other.



Structure 1



Structure 2

(2)

(c) Propylamine, $CH_3CH_2CH_2NH_2$, can be formed either by nucleophilic substitution or by reduction.

(i) Draw the structure of a compound which can undergo nucleophilic substitution to form propylamine.

(ii) Draw the structure of the nitrile which can be reduced to form propylamine.

(iii) State and explain which of the two routes to propylamine, by nucleophilic substitution or by reduction, gives the less pure product. Draw the structure of a compound formed as an impurity.

Route giving the less pure product .....

Explanation .....

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Structure of an impurity

(5)
(Total 15 marks)

Q4. This question is about the primary amine $CH_3CH_2CH_2NH_2$

(a) The amine $CH_3CH_2CH_2NH_2$ reacts with CH_3COCl

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

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(6)

(b) Isomers of $CH_3CH_2CH_2NH_2$ include another primary amine, a secondary amine and a tertiary amine.

(i) Draw the structures of these **three** isomers.
Label each structure as primary, secondary or tertiary.

(3)

(ii) Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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(2)

(c) The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route **A** is a two-stage process and starts from CH_3CH_2Br.

Route **B** is a one-stage process and starts from $CH_3CH_2CH_2Br$.

(i) Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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(7)

(ii) Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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(2)
(Total 20 marks)

Q1. (a) Name the compound $(CH_3)_2NH$

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(1)

(b) $(CH_3)_2NH$ can be formed by the reaction of an excess of CH_3NH_2 with CH_3Br. Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(5)

(c) Name the type of compound produced when a large excess of CH_3Br reacts with CH_3NH_2 Give a use for this type of compound.

Type of compound .....

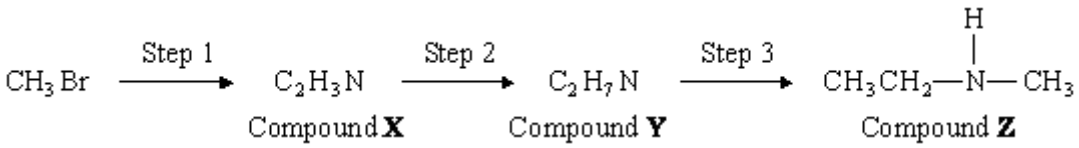
Use .....

(2)

(d) Draw the structures of the two compounds formed in the reaction of CH_3NH_2 with ethanoic anhydride.

(2)
(Total 10 marks)

Q2. Compound **Z** can be formed via compounds **X** and **Y** in the three step synthesis shown below.



Identify compounds **X** and **Y** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **Z** is an example.

Compound **Z** reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

(Total 9 marks)

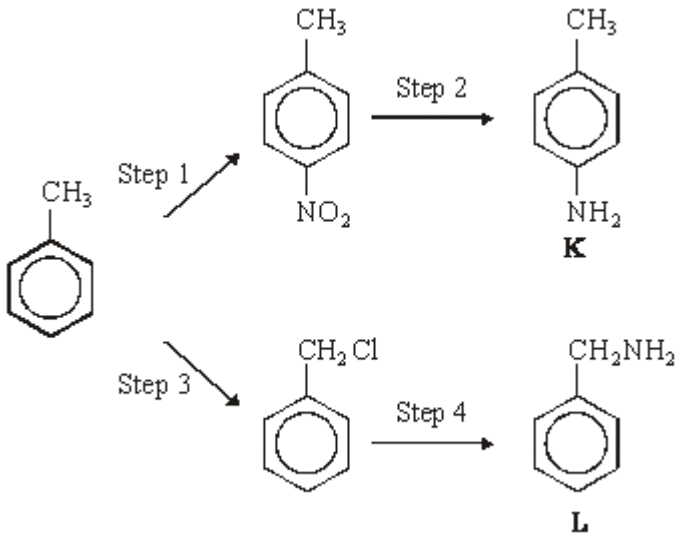
Q3. (a) Outline a mechanism for the formation of ethylamine from bromoethane. State why the ethylamine formed is contaminated with other amines. Suggest how the reaction conditions could be modified to minimise this contamination.

(6)

(b) Suggest one reason why phenylamine cannot be prepared from bromobenzene in a similar way. Outline a synthesis of phenylamine from benzene. In your answer you should give reagents and conditions for each step, but equations and mechanisms are not required.

(5)
(Total 11 marks)

Q4. The following reaction scheme shows the formation of two amines, **K** and **L**, from methylbenzene.



(a) (i) Give the reagents needed to carry out Step 1. Write an equation for the formation from these reagents of the inorganic species which reacts with methylbenzene.

Reagents .....

Equation .....

(ii) Name and outline a mechanism for the reaction between this inorganic species and methylbenzene.

Name of mechanism .....

Mechanism

(7)

(b) Give a suitable reagent or combination of reagents for Step 2.

.....

(1)

(c) (i) Give the reagent for Step 4 and state a condition to ensure that the primary amine is the major product.

Reagent .....

Condition .....

(ii) Name and outline a mechanism for Step 4.

Name of mechanism .....

Mechanism

(7)
(Total 15 marks)

Q5. (a) Name and outline a mechanism for the formation of butylamine, $CH_3CH_2CH_2CH_2NH_2$, by the reaction of ammonia with 1-bromobutane, $CH_3CH_2CH_2CH_2Br$.

Name of mechanism .....

Mechanism

(5)

(b) Butylamine can also be prepared in a two-step synthesis starting from 1-bromopropane, $CH_3CH_2CH_2Br$. Write an equation for each of the two steps in this synthesis.

Step 1

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Step 2

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(3)

(c) (i) Explain why butylamine is a stronger base than ammonia.

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(ii) Identify a substance that could be added to aqueous butylamine to produce a basic buffer solution.

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(3)

(d) Draw the structure of a tertiary amine which is an isomer of butylamine.

(1)
(Total 12 marks)

Q1. This question is about the primary amine $CH_3CH_2CH_2NH_2$

(a) The amine $CH_3CH_2CH_2NH_2$ reacts with CH_3COCl

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

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(6)

(b) Isomers of $CH_3CH_2CH_2NH_2$ include another primary amine, a secondary amine and a tertiary amine.

(i) Draw the structures of these **three** isomers.
Label each structure as primary, secondary or tertiary.

(3)

(ii) Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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(2)

(c) The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route **A** is a two-stage process and starts from CH_3CH_2Br.

Route **B** is a one-stage process and starts from $CH_3CH_2CH_2Br$.

(i) Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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(7)

(ii) Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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(2)
(Total 20 marks)

Q2. Each of the following conversions involves reduction of the starting material.

(a) Consider the following conversion.



Identify a reducing agent for this conversion.

Write a balanced equation for the reaction using molecular formulae for the nitrogen-containing compounds and [H] for the reducing agent.

Draw the repeating unit of the polymer formed by the product of this reaction with benzene-1,4-dicarboxylic acid.

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(Extra space) .....

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(5)

(b) Consider the following conversion.



Identify a reducing agent for this conversion.

State the empirical formula of the product.

State the bond angle between the carbon atoms in the starting material and the bond angle between the carbon atoms in the product.

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(4)

(c) The reducing agent in the following conversion is $NaBH_4$



(i) Name and outline a mechanism for the reaction.

Name of mechanism .....

Mechanism

(5)

(ii) By considering the mechanism of this reaction, explain why the product formed is optically inactive.

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(3)
(Total 17 marks)

Q3. The amide or peptide link is found in synthetic polyamides and also in naturally occurring proteins.

(a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2)

(ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(Extra space) .....

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(3)

(b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism.....

Mechanism

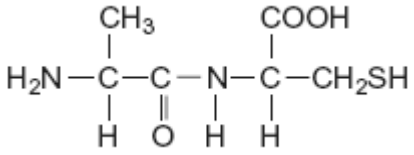
(5)

(ii) Give the name of the product containing an amide linkage that is formed in the reaction in part (b) (i).

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(1)

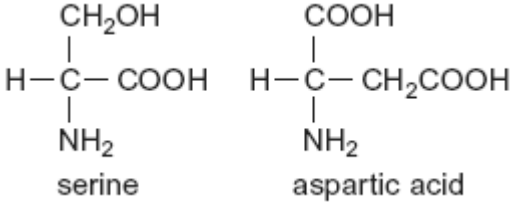
(c) The dipeptide shown below is formed from two different amino acids.



Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1)

(d) The amino acids serine and aspartic acid are shown below.



(i) Give the IUPAC name of serine.

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(1)

(ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1)

(iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

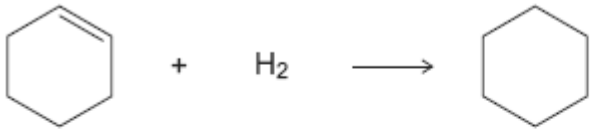
(1)

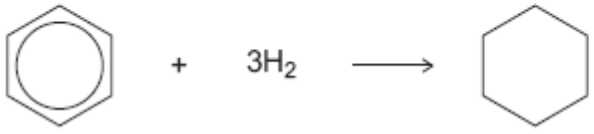
(iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

(1)
(Total 16 marks)

Q1. The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

(a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.





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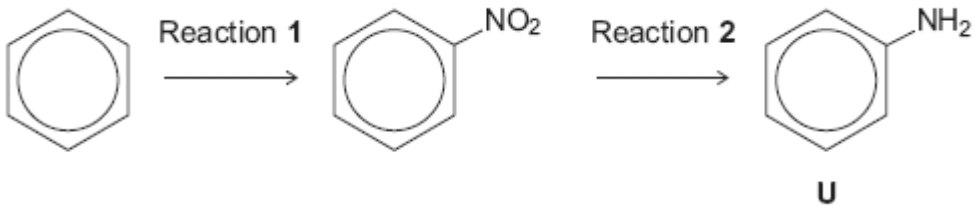
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(4)

(b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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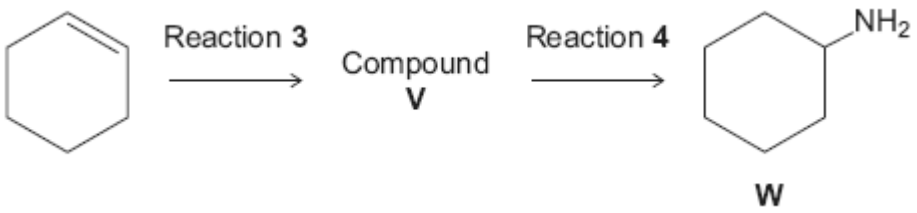
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(6)

(c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(d) Explain why amine **U** is a weaker base than amine **W**.

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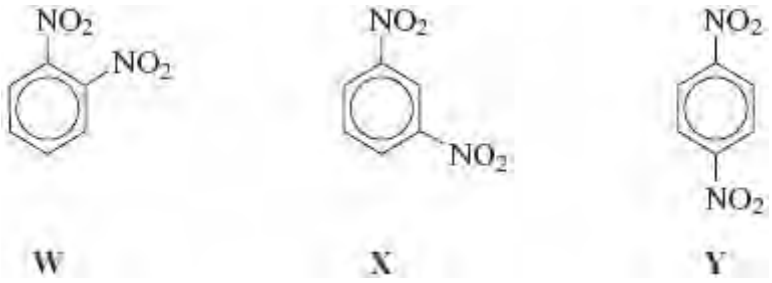
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(3)
(Total 19 marks)

Q2. Three isomers of $C_6H_4(NO_2)_2$ are shown below.



(a) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of each isomer.

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(3)

(ii) Draw the displayed formula of the compound used as a standard in recording these spectra.

(1)

(b) Isomer **X** is prepared from nitrobenzene by reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.

The two acids react to form an inorganic species that reacts with nitrobenzene to form **X**.

(i) Give the formula of this inorganic species formed from the two acids and write an equation to show its formation.

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(2)

(ii) Name and outline a mechanism for the reaction of this inorganic species with nitrobenzene to form **X**.

(4)

(c) Isomer **Y** is used in the production of the polymer Kevlar.

Y is first reduced to the diamine shown below.



(i) Identify a suitable reagent or mixture of reagents for the reduction of **Y** to form this diamine. Write an equation for this reaction using [H] to represent the reducing agent.

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(2)

(ii) This diamine is then reacted with benzene-1, 4-dicarboxylic acid to form Kevlar.
Draw the repeating unit of Kevlar.

(2)

(iii) Kevlar can be used as the inner lining of bicycle tyres. The rubber used for the outer part of the tyre is made of polymerised alkenes.

State the difference in the biodegradability of Kevlar compared to that of rubber made of polymerised alkenes.

Use your knowledge of the bonding in these polymer molecules to explain this difference.

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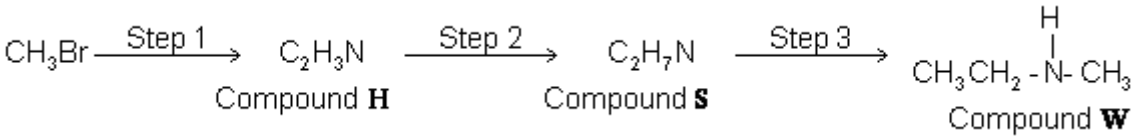
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(4)
(Total 18 marks)

Q3. Compound **W** can be formed via compounds **H** and **S** in the three-step synthesis

shown below.



Identify compounds **H** and **S** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **W** is an example.

W reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

(Total 9 marks)

Q4. (a) Name and outline a mechanism for the reaction of $CH_3CH_2NH_2$ with CH_3CH_2COCl

Name the amide formed.

(6)

(b) Haloalkanes such as CH_3Cl are used in organic synthesis.

Outline a three-step synthesis of $CH_3CH_2NH_2$ starting from methane. Your first step should involve the formation of CH_3Cl

In your answer, identify the product of the second step and give the reagents and conditions for each step.

Equations and mechanisms are **not** required.

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(6)
(Total 12 marks)