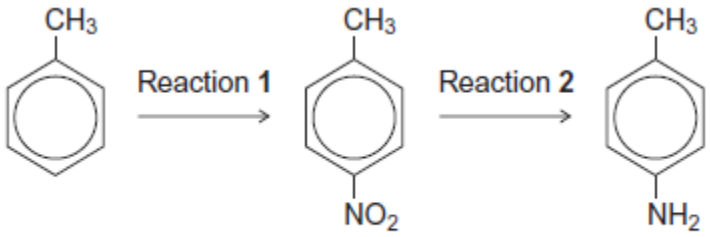
1 Consider the following reaction sequence starting from methylbenzene.



J

(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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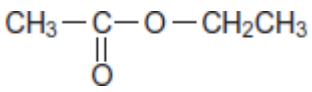
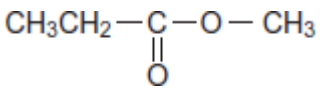
(3)
(Total 11 marks)

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

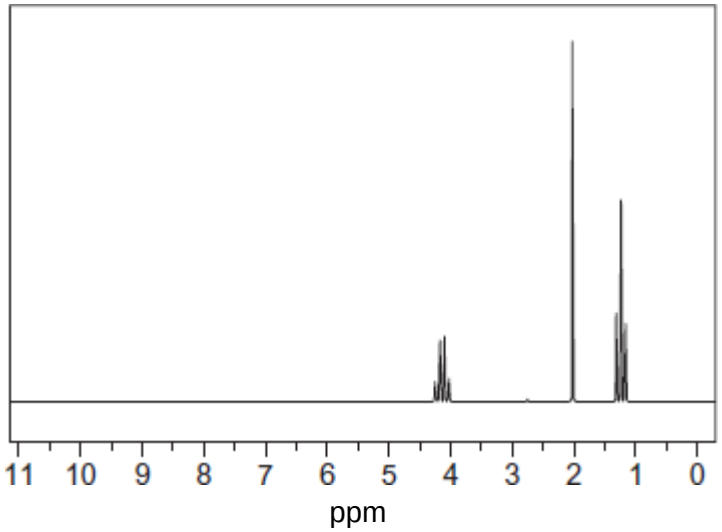


Ester 1



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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(3)
(Total 11 marks)

3 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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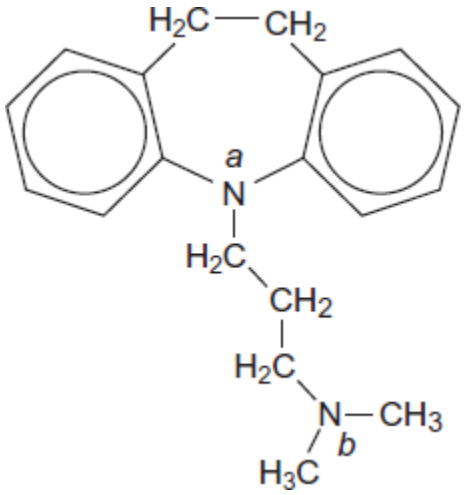
(2)
(Total 20 marks)

4 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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(2)

(Total 5 marks)

5 Ammonia and methylamine were dissolved in separate samples of water. The two solutions had equal molar concentrations.

State **one** simple method, other than smell, of distinguishing these solutions.
State what you would observe.

Method .....

Observation .....

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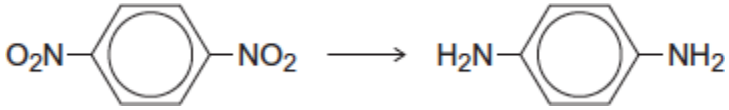
(Total 2 marks)

6 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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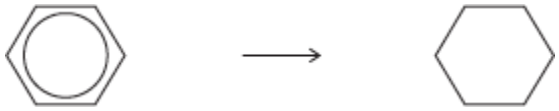
(5)

(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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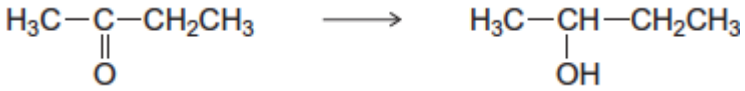
(4)

(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)

7 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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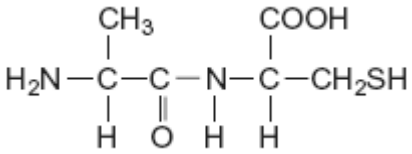
(1)

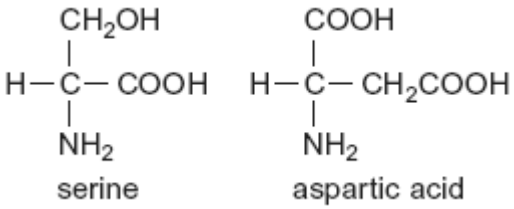
(c) The dipeptide shown below is formed from two different amino acids.



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.

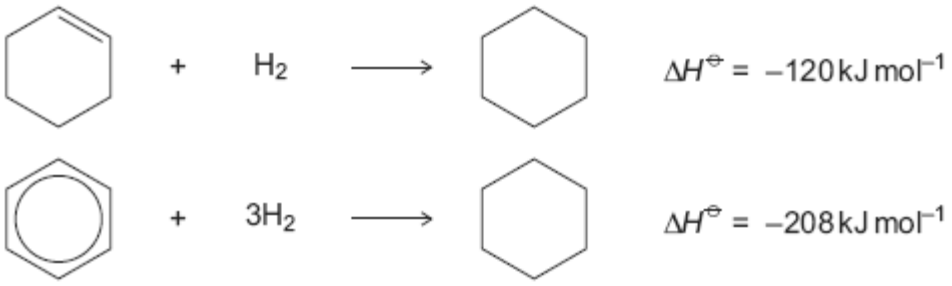
(1)

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

(1)
(Total 16 marks)

8 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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(Extra space) .....

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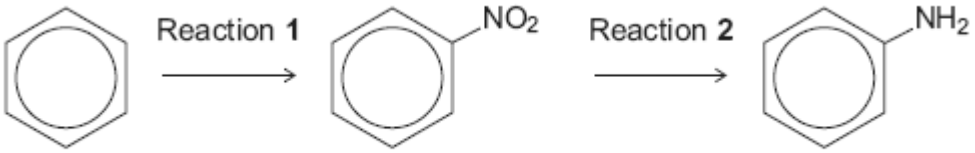
(4)

(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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(Extra space) .....

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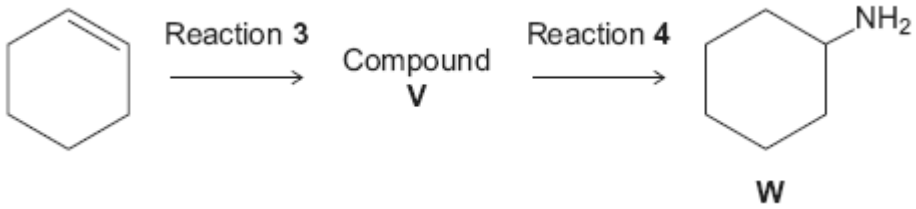
(6)

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



W

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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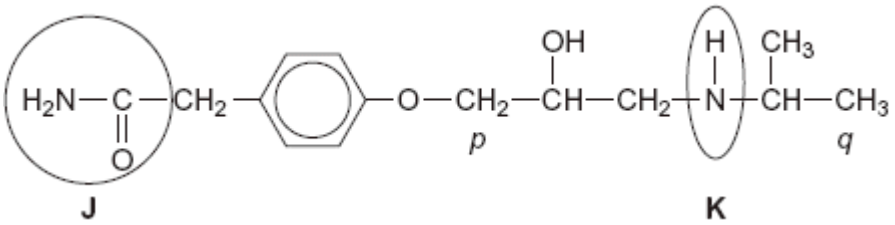
(3)
(Total 19 marks)

9 Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



(a) Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** .....

Functional group labelled **K** .....

(2)

(b) The ^{1}H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the ^{1}H n.m.r. spectrum is produced by the CH_2 group labelled *p* in the structure of atenolol.
Use **Table 2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values .....

Name of splitting pattern ……

(2)

(c) N.m.r. spectra are recorded using samples in solution.

The ^{1}H n.m.r. spectrum was recorded using a solution of atenolol in $CDCl_3$

(i) Suggest why $CDCl_3$ and **not** $CHCl_3$ was used as the solvent.

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(1)

(ii) Suggest why $CDCl_3$ is a more effective solvent than CCl_4 for polar molecules such as atenolol.

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(1)

(d) The ^{13}C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the ^{13}C n.m.r. spectrum of atenolol.

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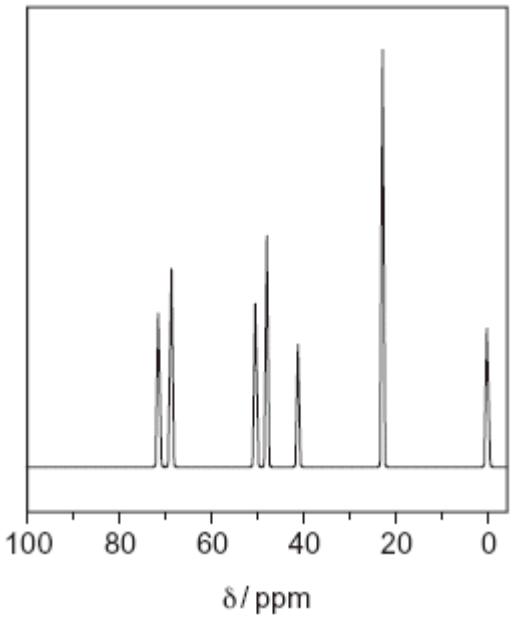
(1)

(e) Part of the ^{13}C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



(i) Give the formula of the compound that is used as a standard and produces the peak at δ = 0 ppm in the spectrum.

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(1)

(ii) One of the peaks in the ^{13}C n.m.r. spectrum above is produced by the CH_3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

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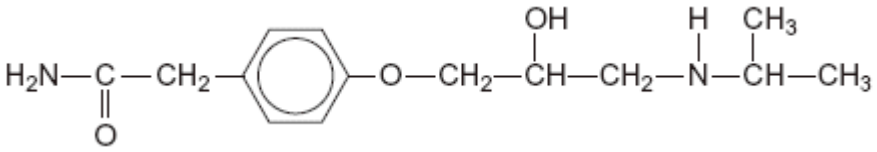
(1)

(iii) There are three CH_2 groups in the structure of atenolol. One of these CH_2 groups produces the peak at δ = 71 in the ^{13}C n.m.r. spectrum above.
Draw a circle around this CH_2 group in the structure of atenolol shown below.



(1)

(f) Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

(i) Suggest a reducing agent that could reduce a ketone to form atenolol.

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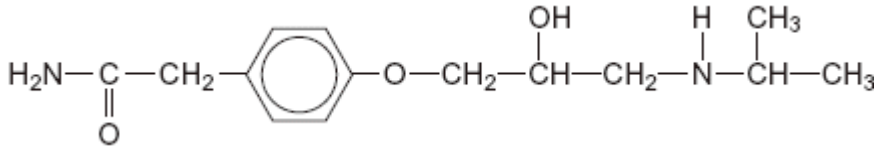
(1)

(ii) Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



(1)

(iii) Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

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(2)

(iv) Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage .....

.....

Disadvantage .....

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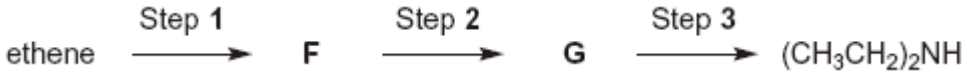
(2)

(Total 16 marks)

10 The compound $(CH_3CH_2)_2NH$ can be made from ethene in a three-step synthesis as shown below.



(a) Name the compound $(CH_3CH_2)_2NH$

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(1)

(b) Identify compounds **F** and **G**.

Compound **F** .....

Compound **G** .....

(2)

(c) For the reactions in Steps **1**, **2** and **3**,

- give a reagent or reagents
- name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

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(6)

(d) Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

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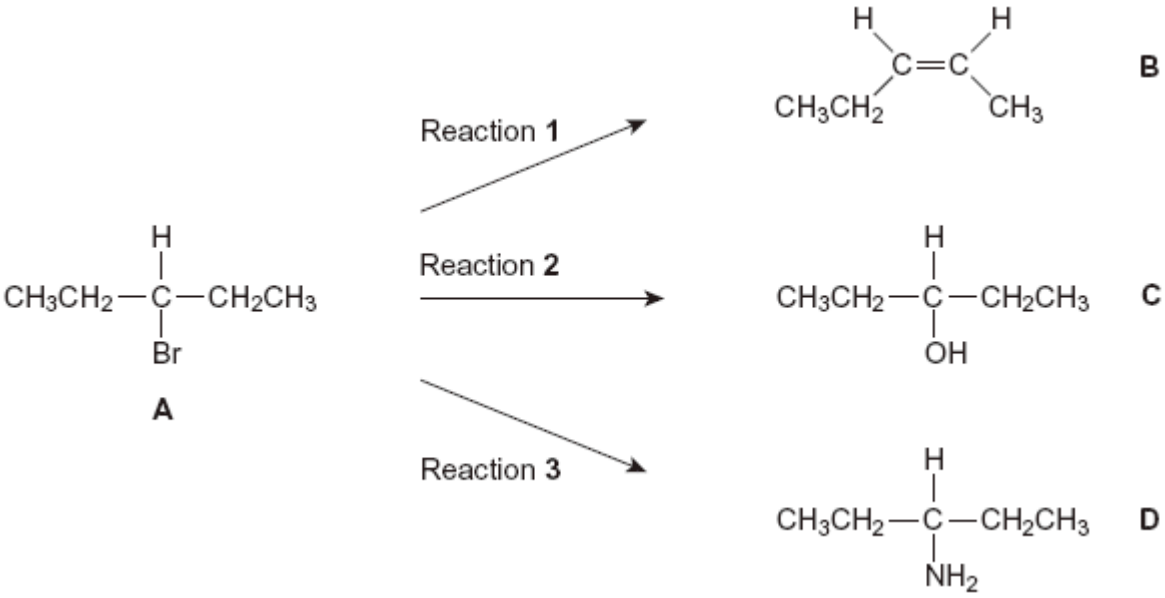
(2)
(Total 11 marks)

11 Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



(a) (i) Draw a **branched-chain** isomer of **A** that exists as optical isomers.

(1)

(ii) Name the type of mechanism in Reaction **1**.

.....

(1)

(iii) Give the full IUPAC name of compound **B**.

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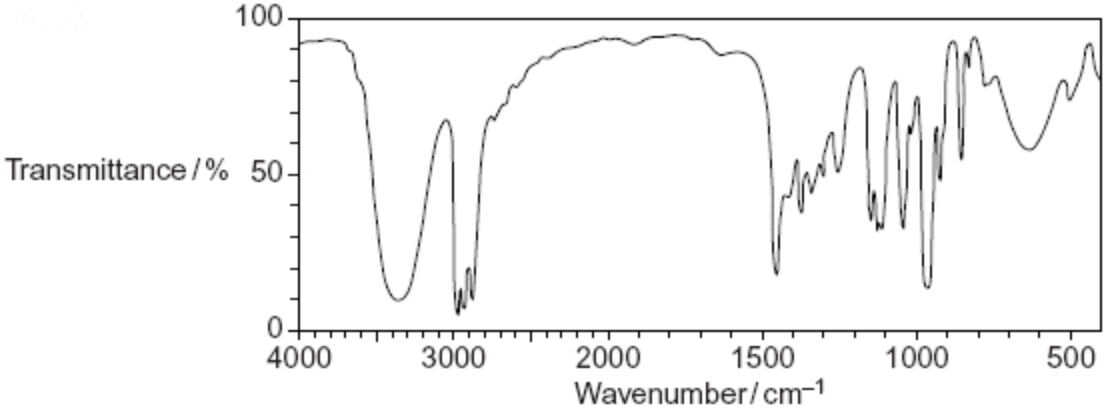
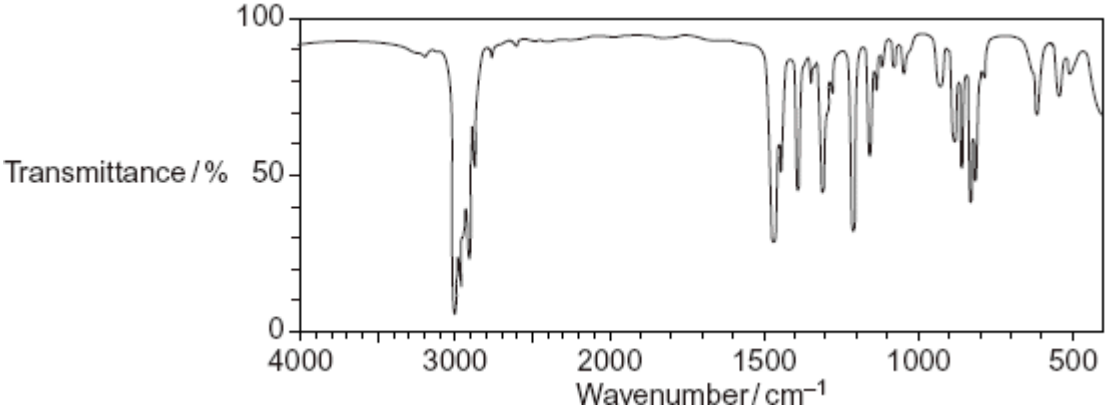
(1)

(b) The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**.
Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

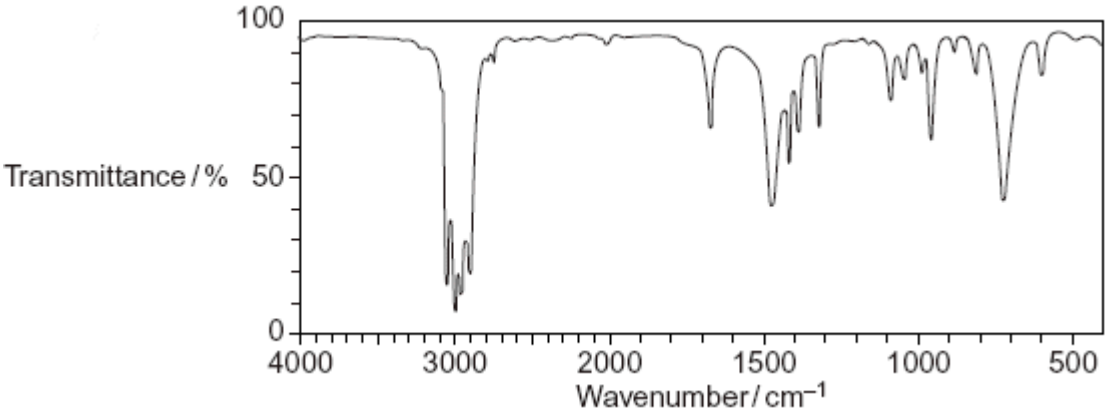
(i)



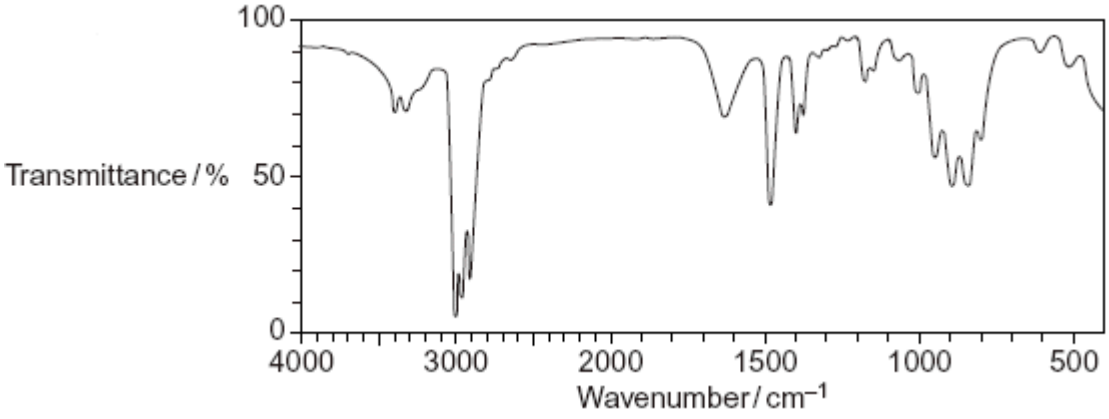
(ii)



(iii)



(iv)



(4)

(c) Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

(2)

(d) (i) Outline a mechanism for Reaction **3**.

(4)

(ii) State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

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(1)

(iii) Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

(1)

(e) **D** is a primary amine which has three peaks in its ^{13}C n.m.r. spectrum.

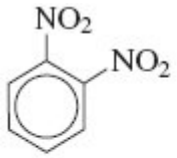
(i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1)

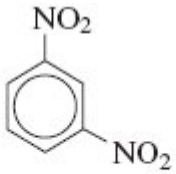
(ii) Another isomer of **D** is a tertiary amine. Its ^{1}H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

(1)
(Total 17 marks)

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



W



X

Y

(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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(4)

(Total 18 marks)

13 (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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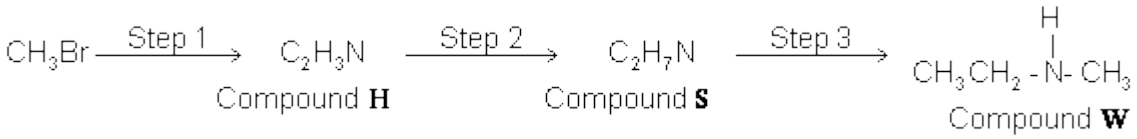
(6)
(Total 12 marks)

14 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.

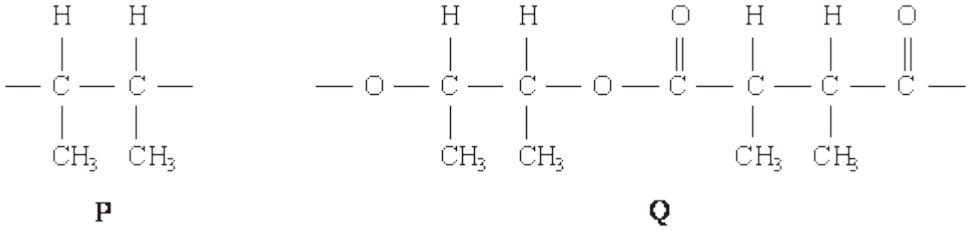
(Total 9 marks)

15 A chemist has discovered that the labels have fallen off four bottles each of which contains a different organic liquid. These liquids are known to be propan-2-ol, propanal, hexene and 1-bromopropane.

Suggest a series of test-tube reactions which a chemist could use to confirm the identities of the four compounds. State the reagents used and the observations expected.

(Total 10 marks)

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



(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 .....

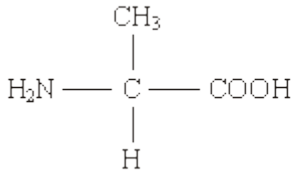
Type of polymerisation .....

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

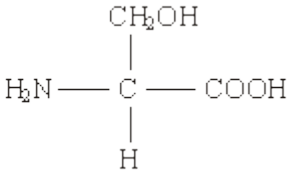
.....

(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 .....

.....

Structure of an impurity

(5)
(Total 15 marks)

17 (a) Name the compound $(CH_3)_2NH$

.....

(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)

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

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

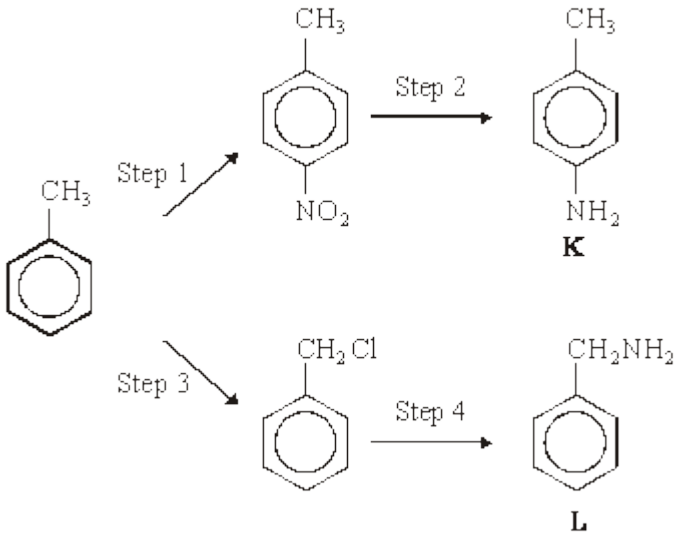
B $AlCl_3 + Cl^- \rightarrow A1C1_4^-$

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)

19 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 .....

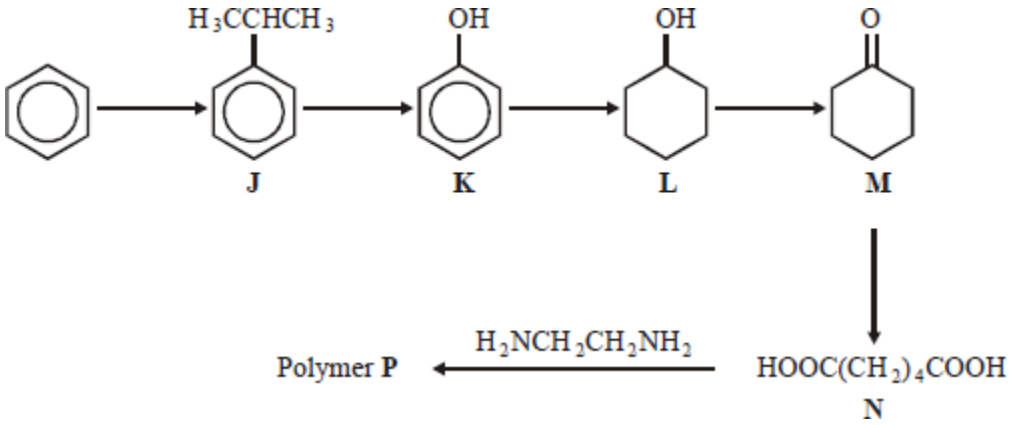
(ii) Name and outline a mechanism for Step 4.

Name of mechanism .....

Mechanism

(7)
(Total 15 marks)

20 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)

21 (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

.....

(3)

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

.....

.....

.....

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

.....

(3)

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

(1)
(Total 12 marks)

22 Which one of the following is **not** a correct general formula for the non-cyclic compounds listed?

A alcohols $C_nH_{2n+2}O$

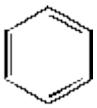
B aldehydes $C_nH_{2n+1}O$

C esters $C_nH_{2n}O_2$

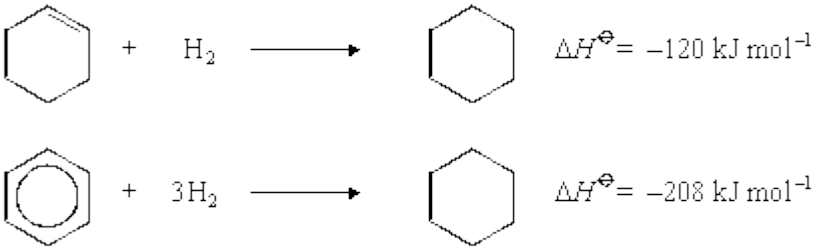
C primary amines $C_nH_{2n+3}N$

(Total 1 mark)

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

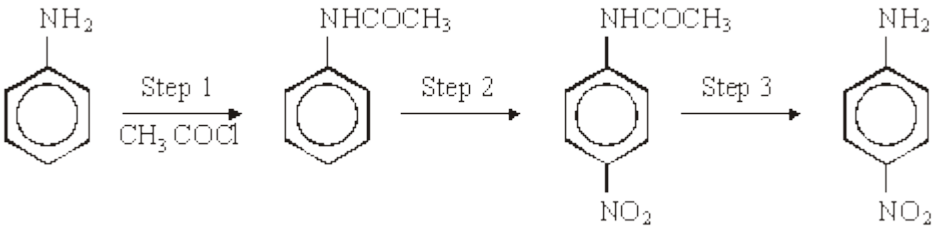


Give a reason for this difference in stability.



(4)

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



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

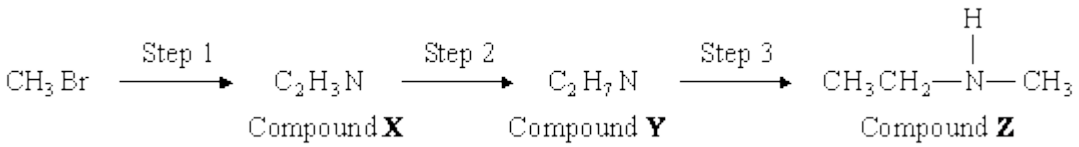
(ii) Name and outline a mechanism for the reaction in Step 1 and name the organic product of Step 1.

(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)

24 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)

25 (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)

26 (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.

.....

.....

.....

(5)

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

.....

.....

.....

(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)

27 (a) Synthetic polyamides are produced by the reaction of dicarboxylic acids with compounds such as $H_2N(CH_2)_6NH_2$

(i) Name the compound $H_2N(CH_2)_6NH_2$

.....

(ii) Give the repeating unit in the polyamide nylon 6,6.

.....

(2)

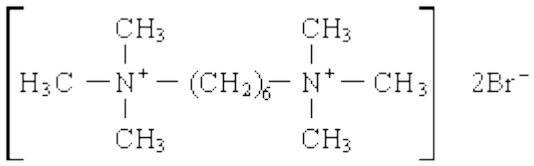
(b) Synthetic polyamides have structures similar to those found in proteins.

(i) Draw the structure of 2-aminopropanoic acid.

(ii) Draw the organic product formed by the condensation of two molecules of 2-aminopropanoic acid.

(2)

(c) Compounds like $H_2N(CH_2)_6NH_2$ are also used to make ionic compounds such as **X**, shown below.



Compound **X**

(i) **X** belongs to the same type of compound as $(CH_3)_4N^+Br^-$
Name this **type** of compound.

.....

(ii) State a reagent which could produce **X** from $H_2N(CH_2)_6NH_2$ and give a necessary condition to ensure that **X** is the major product.

Reagent .....

Condition .....

(iii) Name the mechanism involved in this reaction to form **X**.

.....

(4)
(Total 8 marks)

1

(a) Electrophilic substitution

Both words needed

Ignore minor misspellings

1

(b) (i) Sn / HCl

OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

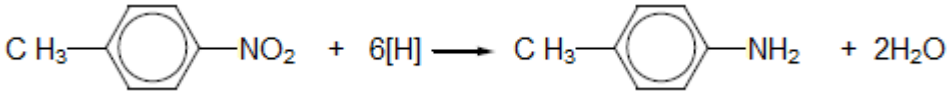
Ignore NaOH after Sn / HCl

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

OR



Allow molecular formulae as structures given

$C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

OR making hair conditioner

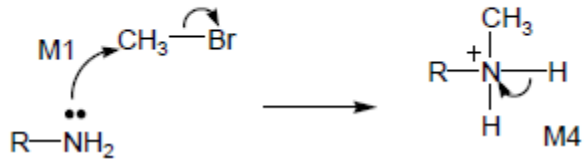
OR making fabric softener

OR making detergents

1

(c)

M2



M3

NO Mark for name of mechanism

Allow SN1

M1 for lone pair on N and arrow to C or mid point of space between N and C

M2 for arrow from bond to Br

M3 for structure of protonated secondary amine

M4 for arrow from bond to N or + on N

For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br^-

4

(d) <u>lone or electron pair on N</u>

If no mention of lone pair CE = 0

If lone pair mentioned but not on N then lose M1 and mark on

M1

1

in **J** spread / delocalised into ring (or not delocalised in K)

Ignore negative inductive effect of benzene

*Allow interacts with **Π** cloud for M2*

M2

1

less available (for protonation or donation in **J**)

M3

OR

in **K** there is a positive inductive effect / electron releasing)

M2

more available (for protonation or donation in **K**)

M3

1

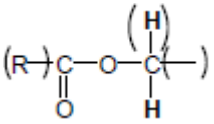
[11]

2

(a) M1 Ester **1**

If Ester 2, can score M3 only.

1

M2 peak at δ = 4.1 due to 

When marking M2 and M3, check any annotation of structures in the stem at the top of the page.

1

M3 (δ = 4.1 peak is) quartet as adjacent / next to / attached to CH_3

1

M4 Other spectrum quartet at δ = 2.1-2.6 (or value in this range)

1

(b) M1 Quaternary (alkyl) ammonium salt / bromide

1

M2 CH_3Br or bromomethane

Penalise contradictory formula and name.

1

M3 Excess (CH_3Br or bromomethane)

Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3.

1

M4 Nucleophilic substitution

Can only score M3 if reagent correct.

Ignore alcohol or ethanol (conditions) or Temp.

1

(c)

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.

If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change

Ignore 'clear', 'nothing'.

Allow colour fades slowly.

Allow 'nvc' for no visible change.

1

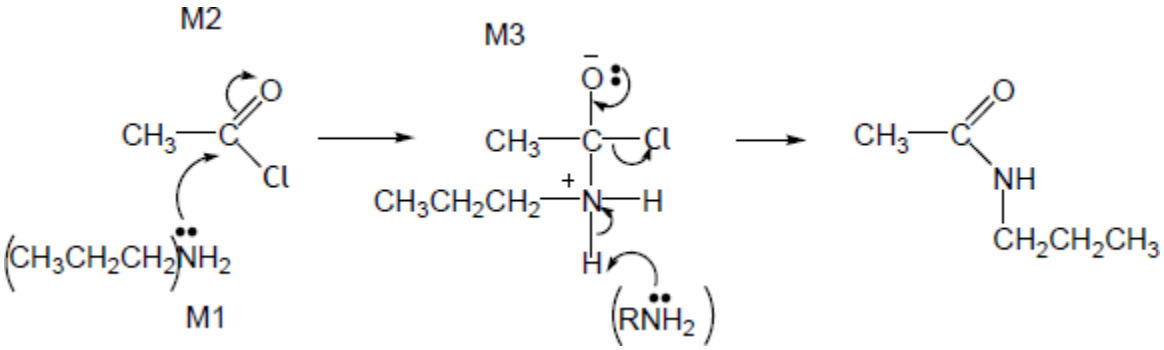
cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[11]

3 (a) (nucleophilic) addition-elimination

1



M4 for 3 arrows and lp

Allow wrong amine in M1 but penalise in M3

Allow C_3H_7 in M3

Minus sign on NH_3 loses M1 (but not M4 if NH_3 also shown here)

- *Allow attack by: $NH_2CH_2CH_2CH_3$*
- *M2 not allowed independent of M1, but allow M1 for correct attack on C^+*
- *+ rather than δ+ on C=O loses M2*
- *If Cl lost with C=O breaking, max 1 for M1*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4*
- *3 arrows in M4 can be shown in two separate steps.*
- *If M3 drawn twice, mark first answer eg ignore missing + if missed off second structure*
- *Only allow M4 after correct / very close M3*
- *For M4, ignore RNH_2 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism,*
- *but ignore HCl shown as a product.*

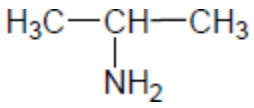
4

<u>N-propylethanamide</u> must be this name even if wrong amine used

NOT N-propylethaneamide

1

(b) (i)



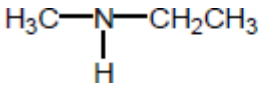
Primary

Not allow ambiguous $C_3H_7NH_2$

BEWARE No mark for the original amine $CH_3CH_2CH_2NH_2$

Label and structure must both be correct for each type to score the mark.

1

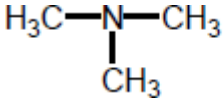


Secondary

Allow C_2H_5

Penalize wrong number of carbons but otherwise correct, first time only.

1



tertiary

1

(ii) Absorption at 3300−3500 (cm^{-1}) in spectrum

Allow trough, peak, spike.

Ignore absorption at 750 − 1100 for C–C bond in secondary - this is within fingerprint region.

Allow any number in this range.

If range missing, no further marks.

If range linked to tertiary, no further marks.

1

N–H (bond) (only) present in secondary amine or not present in tertiary amine

OR

This peak or N–H absorption (only) present in spectrum of secondary amine or not present in spectrum of tertiary amine

1

(c) (i) M1 Route **A**: stage 1 KCN

Apply list principle for extra reagents or catalysts
NOT HCN NOT KCN / acid Not KCN / HCN

1

M2 Aqueous or ethanolic

M2 only scores after correct M1
ignore warm; acid here loses M1 & M2

1

M3 Route **A** Intermediate CH_3CH_2CN or propanenitrile

If M3 intermediate wrong, max 2 for M1 & M2 ie no mark for stage 2

Name alone must be exactly correct to gain M1 but mark on if name close

But if M3 intermediate close, eg "nitrile" or wrong nitrile, can award marks in stage 2

correct formula gains M1 (ignore name if close)

If stage 1 correct and intermediate is missing, can award marks in stage 2

contradiction of name and formula loses mark

stage 1 wrong & intermediate missing, no marks.

1

M4 Route **A**: stage 2 H_2

H loses M4 but mark on

$LiAlH_4$

Apply list principle for extra reagents or catalysts.

M5 only scores after correct M4

Not $NaBH_4$ not Sn or Fe / HCl

Allow (dil) acid after but not with $LiAlH_4$

Penalise conc acid.

1

M5 Ni or Pt or Pd

ether

1

M6 Route **B** NH_3

With acid loses M6 & M7

Apply list principle for extra reagents or catalysts.

1

M7 Excess NH_3

Ignore conc, ignore high P, ignore solvent.

1

(ii) Route **A** disadv Toxic / poisonous KCN or cyanide or CN^- or HCN

Expensive $LiAlH_4$
ignore acidified

OR lower <u>yield</u> because 2 steps

Allow H_2 flammable / explosive etc.

Not just dangerous.

Ignore time reasons.

1

Route **B** disadv Further reaction / substitution likely

Allow impure product.

1

[20]

4

(a) M1 Lone pair on N labelled b more available / more able to be donated than lone pair on N labelled *a*

Ignore N(b) more readily accepts protons.

Ignore N(b) is stronger base.

1

M2 lp or electrons or electron density on N labelled *a:*

delocalized into (benzene) ring

QoL

1

M3 lp or electrons or electron density on N labelled *b:*

methyl / alkyl groups electron releasing or donating or (positive) inductive effect or push electrons or electron density

QoL

1

(b) $C_{19}H_{24}N_2$

Any order.

1

11

1

[5]

5

Measure pH with a meter

Chemical indicators not allowed for M1 (allow mark for M2 if student describes differences in pHs but not for differences in colours).

1

Methylamine would have a higher pH / ammonia would have a lower pH

Use of $CuSO_4$ not allowed.

1

[2]

6

(a) Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid

Allow H_2 (Ni / Pt) but penalise wrong metal

But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH

1

Equation must use molecular formulae

$C_6H_4N_2O_4 + 12\ [H]$

12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

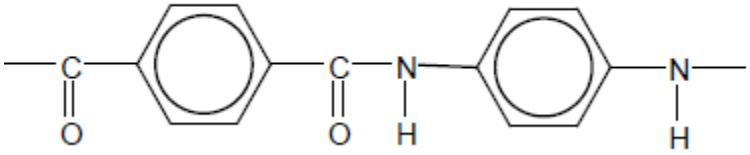
1

$\rightarrow C_6H_8N_2 + 4H_2O$

Allow .... + $6H_2$ if H_2 / Ni used

Allow −CONH− or −COHN− or $-C_6H_4-$

1



Mark two halves separately: lose 1 each for

- *error in diamine part*
- *error in diacid part*
- *error in peptide link*
- *missing trailing bonds at one or both ends*
- *either or both of H or OH on ends*

Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal

NOT Sn / HCl, $NaBH_4$ etc.

1

CH_2

1

In benzene 120°

1

In cyclohexane 109° 28’ or 109½°

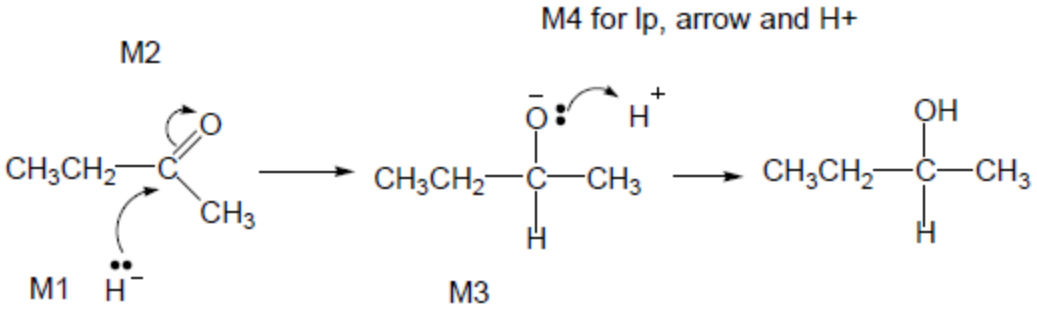
Allow 108° - 110°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

1



- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *M3 is for correct structure including minus sign but lone pair is part of M4*
- *Allow C_2H_5*
- *M1 and M4 include lp and curly arrow*
- *Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)*

4

(ii) M1 Planar C=O (bond / group)

Not just planar molecule

1

M2 Attack (equally likely) from either side

Not just planar bond without reference to carbonyl

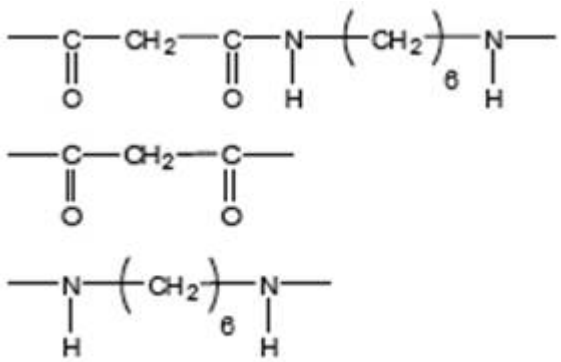
1

M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely

1

[17]

7 (a) (i)



Allow –CONH- or - COHN -

Mark two halves separately

lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends

1

Not allow –(C_6H_{12})–

Ignore n

1

(ii) **M1** in polyamides - H bonding

1

M2 in polyalkenes - van der Waals forces

Penalise forces between atoms or van der Waals bonds

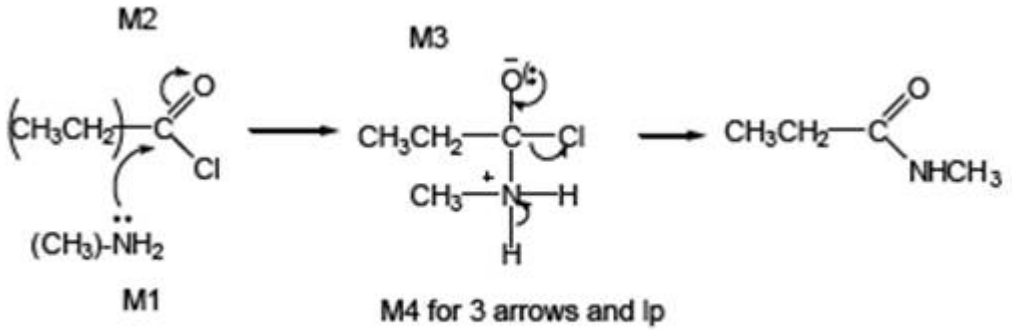
1

M3 Stronger forces (of attraction) in polyamides
Or H bonding is stronger
(must be a comparison of correct forces to score M3)

Do not award if refer to stronger bonds

1

(b) (i) (nucleophilic) addition elimination



M1

M4 for 3 arrows and lp

Not allow N–H_2

*Minus sign on NH_2 loses **M1***

1

*M2 not allowed independent of **M1**, but allow **M1** for correct attack on C+*

*+ rather than δ+ on C=O loses **M2***

*If Cl lost with C=O breaking, max 1 for **M1***

***M3** for correct structure <u>with charges</u> but*

*lp on O is part of **M4***

*only allow **M4** after correct/ very close M3*

For M4, ignore NH_3 removing H^+ but lose

***M4** for Cl removing H^+ in mechanism,*

but ignore HCl as a product

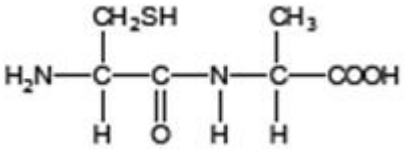
4

(ii) <u>N-methylpropanamide</u>

Not N-methylpropaneamide

1

(c)



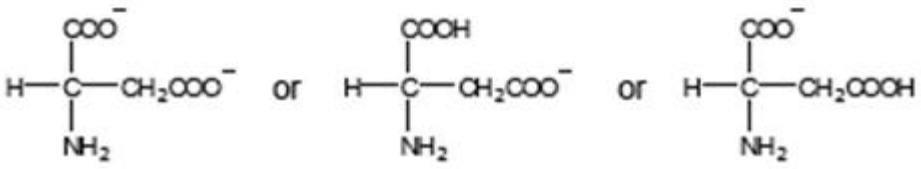
Allow –CONH– or –COHN–

1

(d) (i) 2-amino-3-hydroxypropanoic acid

1

(ii)



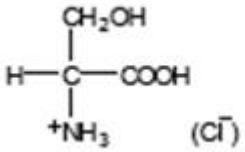
Must be salts of aspartic acid

allow $–CO_2^-$

allow $NH_2–$

1

(iii) Penalise use of aspartic acid once in d(iii) and d(iv)



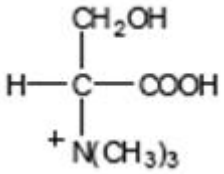
allow $–CO_2H$

allow $^+NH_3–$

don't penalize position of + on NH_3

1

(iv) Penalise use of aspartic acid once in d(iii) and d(iv)



(Br^-)

allow $–CO_2^-$

must show C-N bond

don't penalize position of + on $N(CH_3)_3$

1

[16]

8

(a) **M1** Benzene is more stable than cyclohexatriene

more stable than cyclohexatriene must be stated or implied

If benzene more stable than cyclohexene, then penalise M1 but mark on

If benzene less stable: can score M2 only

1

M2 Expected ΔHº hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected ΔHº hydrog is three times the ΔHº hydrog of cyclohexene

1

M3 Actual ΔHº hydrogenation of benzene is

152 kJ mol^{-1} (less exothermic)

or 152 kJ mol^{-1} different from expected

Ignore energy needed

1

M4 Because of delocalisation or electrons spread out or resonance

1

(b) **No mark for name of mechanism**

Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation

1

$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$

OR

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

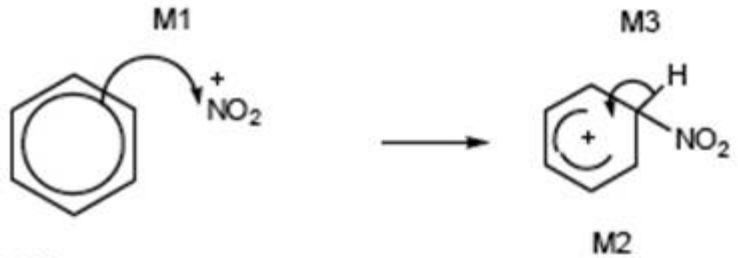
OR via two equations

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$

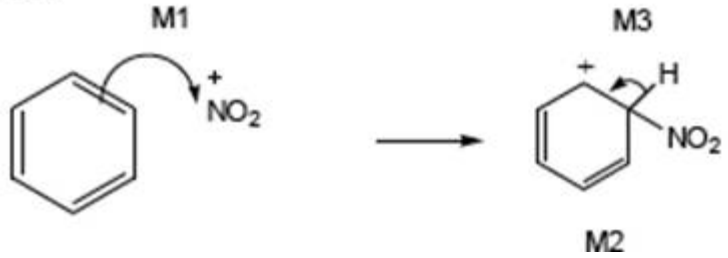
$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



OR



M1 arrow from within hexagon to N or + on N

Allow NO_2^+ in mechanism

horseshoe must not extend beyond C2 to C6 but can be smaller

+ not too close to C1

M3 arrow into hexagon unless Kekule

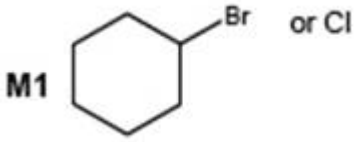
allow M3 arrow independent of M2 structure

ignore base removing H in M3

+ on H in intermediate loses M2 not M3

3

(c) **If intermediate compound V is wrong or not shown, max 4 for 8(c)**



or chlorocyclohexane or bromocyclohexane

1

Reaction 3

M2 HBr

1

M3 Electrophilic addition

Allow M2 and M3 independent of each other

1

Reaction 4

M4 Ammonia if wrong do not gain M5

1

Allow M4 and M6 independent of each other

M5 Excess ammonia or sealed in a tube or under pressure

1

If CE e.g. acid conditions, lose M4 and M5

M6 Nucleophilic substitution

1

(d) Lone or electron pair on N

No marks if reference to "lone pair on N" missing

1

Delocalised or spread into ring in U

1

Less available (to accept protons) or less able to donate (to H^+)

1

[19]

9

(a) **J** (acid) amide

not peptide, not N-substituted amide

1

K (secondary) amine or amino

penalise primary or tertiary
allow N-substituted amine

1

(b) (δ =) 3.1-3.9

1

doublet **OR** duplet

Not 3.7 – 4.1

Not secondary
name required not the number 2

1

(c) (i) Solvent must be proton-free

OR $CHCl_3$ has protons or has H or gives a peak

1

(ii) $CDCl_3$ is polar **OR** CCl_4 is non-polar

1

(d) 11 **OR** eleven

1

(e) (i) $Si(CH_3)_4$ **OR** SiC_4H_{12}

ignore TMS

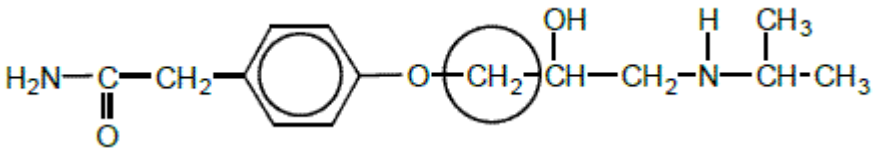
1

(ii) a single number or a range within 21-25

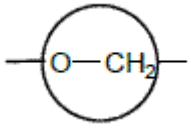
penalise anything outside this range

1

(iii)



allow ring around the C only and also allow



1

(f) (i) $NaBH_4$

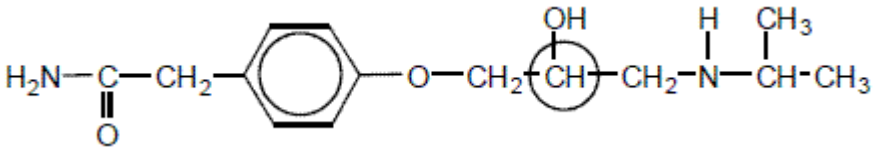
ignore name if formula correct

ignore solvent

allow $LiAlH_4$ Zn/HCl Sn/HCl H_2/Ni H_2/Pt

1

(ii)



allow ring around the C only

1

(iii) (plane) polarised light **OR** light in a polarimeter

1

polarised light is not rotated or is unaffected

penalise bent/diffracted/deflected/reflected

Not just solution is optically inactive

1

(iv) **adv** cheaper medicine due to cost or difficulty <u>of separation</u> or both can lower blood pressure

OR more effective/beneficial <u>with a reason</u>

or no need to separate

1

disadv may be side effects from one enantiomer in the mixture or only half the product works or one enantiomer may be ineffective or double dose required

1

[16]

10 (a) diethylamine **OR** ethyl ethanamine **OR** ethyl aminoethane

ignore N–

1

(b) For (b) and (c)

There are three valid routes for this synthesis called
Routes **A**, **B** and **C** below

- Decide which route fits the answer best (this may not be the best for part b) to give the candidate the best possible overall mark.
- Mark part (b)
- For this best route mark the mechanism and reagent independently
- Migration from one route to another is not allowed
- Either name or formula is allowed in every case.
- Ignore conditions unless they are incorrect.

	Route A	Route B	Route C	
F	CH_3CH_2Br or CH_3CH_2Cl	C_2H_6	CH_3CH_2OH	1
G	$CH_3CH_2NH_2$ ethylamine OR ethanamine OR aminoethane	CH_3CH_2Br OR CH_3CH_2Cl	CH_3CH_2Br OR CH_3CH_2Cl	1

(c)

		Route A	Route B	Route C	
Step 1	Reagent(s)	HBr **OR** HCl	$\underline{H_2/Ni}$ (Not $NaBH_4$)	H_2O & H_3PO_4 **OR** H_2O & H_2SO_4	**1**
	Mechanism	Electrophilic addition	addition (allow electrophilic **OR** catalytic but not nucleophilic) ignore hydrogenation	Electrophilic addition	**1**
Step 2	Reagent(s)	NH_3	Cl_2 **OR** Br_2	HBr OR KBr & H_2SO_4 **OR** PCl_3 **OR** PCl_5 **OR** $SOCl_2$	**1**
	Mechanism	Nucleophilic substitution	(free) radical substitution	Nucleophilic substitution	**1**
Step 3	Reagent(s)	CH_3CH_2Br **OR** CH_3CH_2Cl	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	**1**
	Mechanism	Nucleophilic substitution	Nucleophilic substitution	Nucleophilic substitution	**1**

(d) tertiary amine **OR** triethylamine **OR** $(CH_3CH_2)_3N$
Quaternary ammonium salt
OR tetraethylammonium bromide **OR** chloride **OR** ion
OR $(CH_3CH_2)_4N^+$ (Br^- **OR** Cl^-)

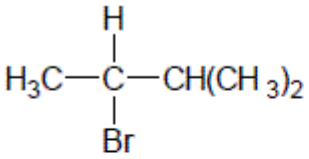
1

further substitution will take place **OR**
diethylamine is a better nucleophile than ethylamine

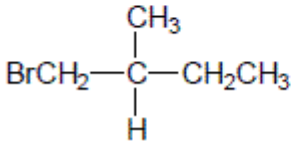
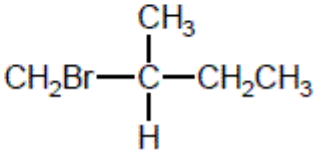
1

[11]

11 (a) (i)



must be **branched** and chiral

or  or 

not allow C_3H_7

allow C_2H_5 bonded to C either way round

1

(ii) elimination

allow base – elimination

but penalise any other qualification

1

(iii) Z-pent-2-ene or cis-pent-2-ene either Z or cis is necessary
(allow Z-2-pentene or cis-2-pentene)

with or without brackets around Z
with or without hyphens

1

(b) (i) C

1

(ii) A

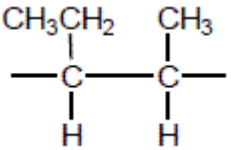
1

(iii) B

1

(iv) D

1

(c) 

allow C_2H_5 bonded via C or H

must have both trailing bonds
ignore brackets or n

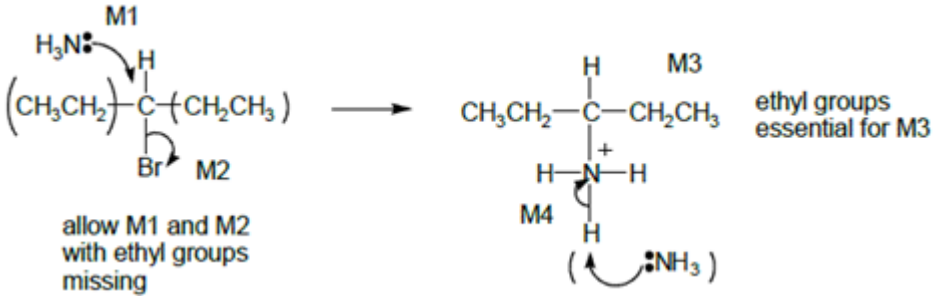
1

addition or radical or step or chain growth

QOL not additional

1

(d) (i)



Allow SN1, i.e M2 first then attack of NH_3 on carbocation.

Allow C_2H_5 in M3 bonded either way

Allow with or without NH_3 to remove H^+ in M4, but lose mark if Br^- used.

ignore δ+ or δ– unless wrong

+ on central C instead of δ + loses M2

4

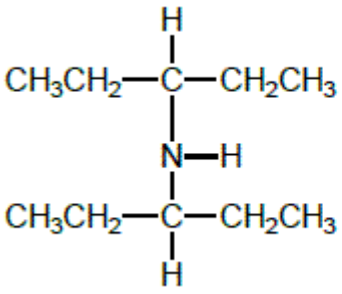
(ii) <u>excess</u> NH_3

ignore reflux

allow conc ammonia in sealed tube

1

(iii)

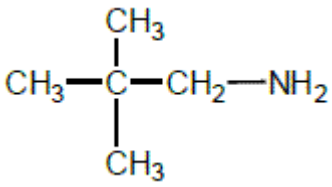


NOT $-C_5H_{11}$

Allow C_2H_5 bonded either way

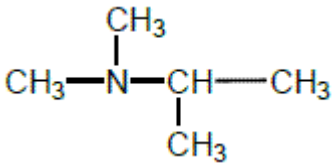
1

(e) (i)



1

(ii)



NOT $(C_2H_5)_2NCH_3$ which is tertiary with 3 peaks but its spectrum has no doublet.

1

[17]

12 (a) (i) **W** 3

1

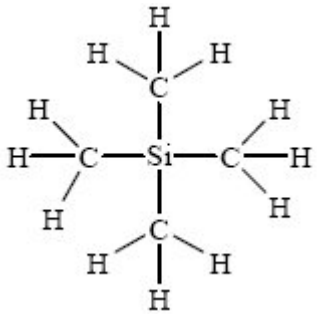
X 4

1

Y 2

1

(ii)



displayed formula shows ALL bonds

1

(b) (i) NO_2^+

allow + anywhere
can score in equation

1

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

1

OR

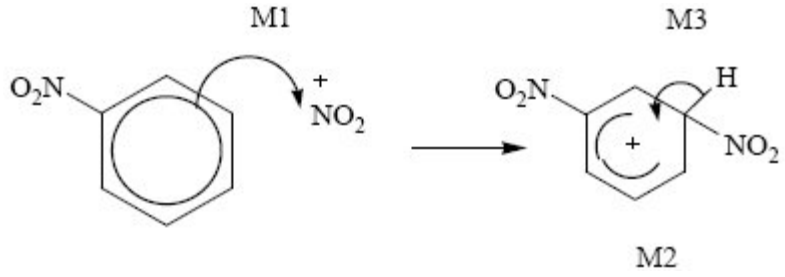
$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

or use two equations via $H_2NO_3^+$

(ii) electrophilic substitution

Not Friedel Crafts

1



Allow Kekule structures

+ must be on N of $^+NO_2$ (which must be correct)

both NO_2 must be correctly positioned and bonded to gain M2

M1 arrow from circle or within it to N or to + on N
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure
ignore base removing H in M3

3

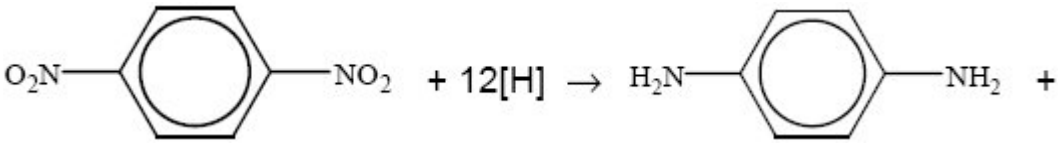
(c) (i) H_2/Ni or H_2/Pt or Sn/HCl or Fe/HCl (conc or dil or neither)

allow dil H_2SO_4

ignore mention of NaOH

Not $NaBH_4$
Not $LiAlH_4$
Not Na/C_2H_5OH
not conc H_2SO_4 or any HNO_3

1

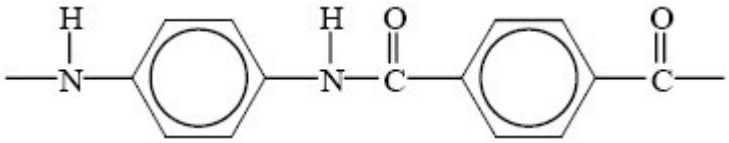


$4H_2O$

Or $6H_2$

allow $C_6H_4(NO_2)_2$ etc ,
allow NO_2– NH_2–
i.e. be lenient on structures, the mark is for balancing equ

1

(ii) 

allow –CONH

ignore $[\ ]_n$ as in polymer

1st mark for correct peptide link

2nd mark for the rest correct including trailing bonds

2

(iii) **M1** Kevlar is <u>biodegradeable</u> but polyalkenes not

allow Kevlar is <u>more</u> biodegradeable

1

M2 Kevlar has <u>polar</u> bonds/is a (poly) amide/has peptide link

comment on structure of Kevlar

1

M3 can be hydrolysed/attacked by nucleophiles/acids/ bases/enzymes

1

M4 polyalkenes <u>non polar</u>/has <u>non-polar</u> bonds

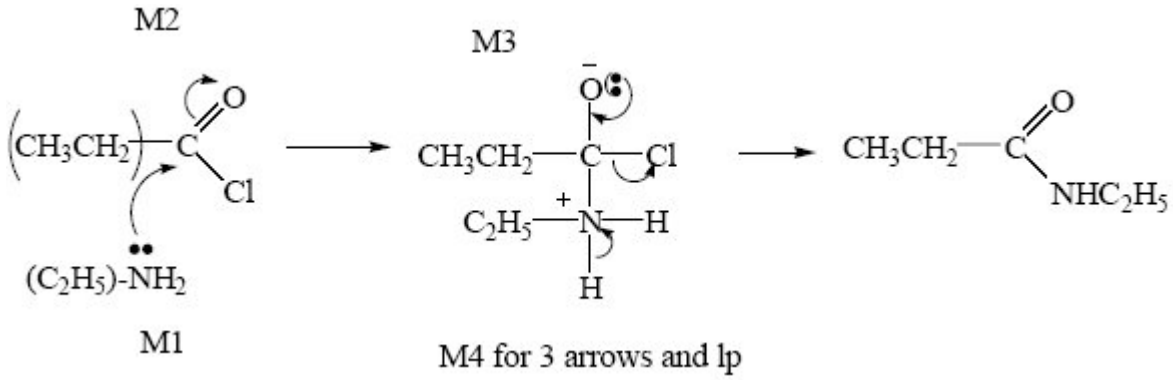
comment on structure of polyalkenes but not just strong bonds

1

[18]

13 (a) (nucleophilic) addition-elimination

1



4

N-ethylpropanamide

minus on NH_2 loses M1
M2 not allowed independent of M1, but allow M1 for correct attack on C+
+C=O loses M2
only allow M4 after correct or very close M3
lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
Not N-ethylpropaneamide

1

(b) CH_3CN or ethan(e)nitrile or ethanonitrile

not ethanitrile
but allow correct formula with ethanitrile

1

for each step wrong or no reagent loses condition mark

contradiction loses mark

1

Step 1 Cl_2
uv or above 300 °C

wrong or no reagent loses condition mark

1

Step 2 KCN

1

aq and alcoholic (both needed)

allow uv light/(sun)light/uv radiation

1

Step 3 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH

not CN^- but mark on
NOT HCN or KCN + acid, and this loses condition mark
NOT $NaBH_4$
Sn/HCl (forms aldehyde!)
ignore conditions

1

[12]

14

H CH_3CN or ethanenitrile **1**

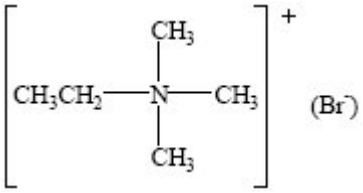
S $CH_3CH_2NH_2$ or ethylamine 1Step 1 KCN **1**

aq/alcoholic **1**

Step 2 H_2 **1**

Ni **1**

W secondary amine **1**



1

nucleophilic substitution **1**

[9]

15 Acidified potassium dichromate(VI)

1

Turns green with propan-2-ol and propanal

1

No reaction with hexene and 1-bromopropane

1

Tollens with propan-2-ol and propanal

1

only propanal gives silver mirror

1

Bromine water

1

Decolourised by hexane

1

No reaction with 1-bromopropane

1

Warm NaOH followed by acidified $AgNO_3$

1

White ppt with 1-bromopropane

1

[10]

16 (a) (i) $CH_3CH=CHCH_3$

1

Addition or radical (**QoL**)

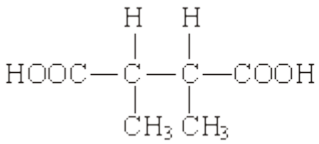
1

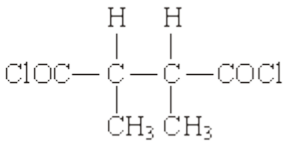
(ii) $CH_3CH(OH)CH(OH)CH_3$ or with no brackets

1

butan(e)–2,3–diol or 2,3–butan(e)diol

1



allow 

1

2,3–dimethylbutan(e)dioic acid 2,3–dimethylbutan(e)dioyl chloride

ignore –1,4–

1

condensation (**QoL**)

1

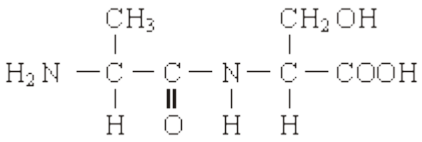
(iii) NaOH or HCl etc or Na_2CO_3

Allow conc sulphuric/nitric

***NOT** water nor acidified water nor weak acids*

1

(b) Structure 1



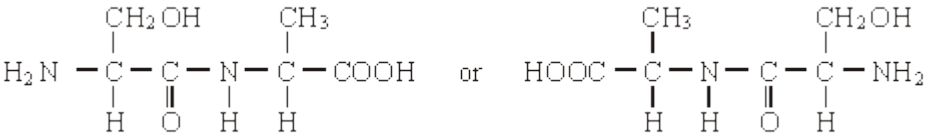
Allow –CONH– and –COHN–

Allow zwitterions

NOT polypeptides/repeating units

1

Structure 2 either of



1

(c) (i) $CH_3CH_2CH_2Br$

allow –Cl, –I

1

(ii) CH_3CH_2CN

1

(iii) (nucleophilic) substitution or from $CH_3CH_2CH_2Br$

if reduction written here, no further marks

1

further substitution/reaction occurs or other products are formed

Allow reduction forms only one product

1

one of

$(CH_3CH_2CH_2)_2NH$

$(CH_3CH_2CH_2)_3N$

$(CH_3CH_2CH_2)_4N^+ Br^-$

Allow salts including NH_4Br

Allow HBr

1

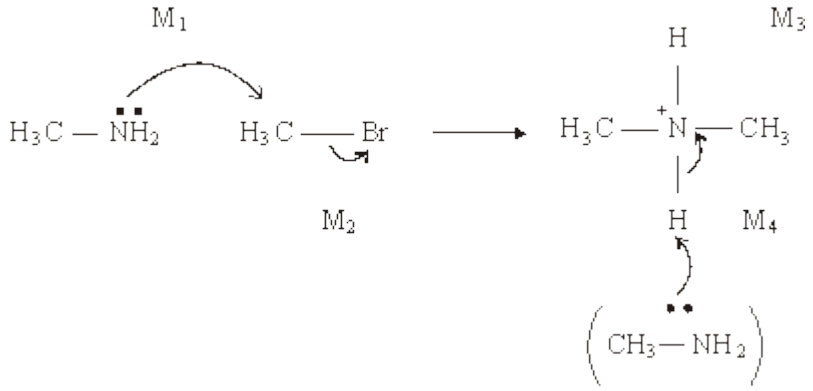
[15]

17 (a) dimethylamine

1

(b) nucleophilic substitution

1



4

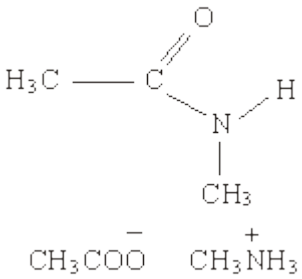
(c) quaternary ammonium salt

1

(cationic) surfactant / bactericide / detergent / fabric softener or conditioner/hair conditioner

1

(d)



(allow CH_3COOH or $CH_3COO^-\ NH_4^+$)

2

[10]

18 D

[1]

19 (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

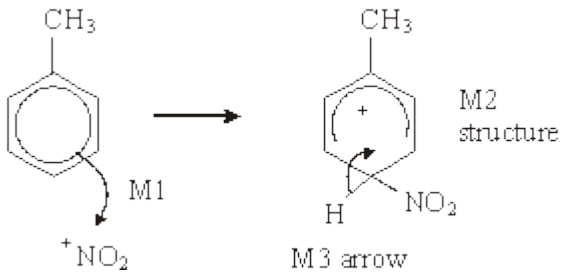
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$

1

(iii) electrophilic substitution CH_3

1



horseshoe must not extend beyond C2 to C6 but can be smaller
+ must not be too close to Cl

3

(b) Sn or Fe / HCl (conc or dil or neither)
or Ni / H_2 not $NaBH_4$ $LiAlH_4$

1

(c) (i) NH_3

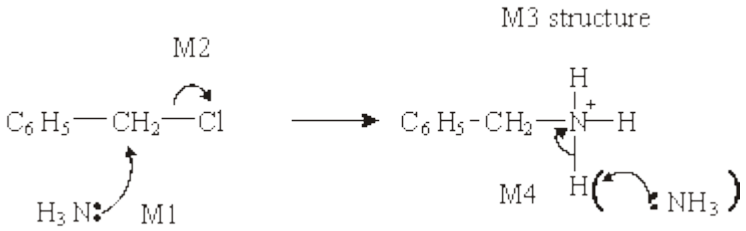
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

1



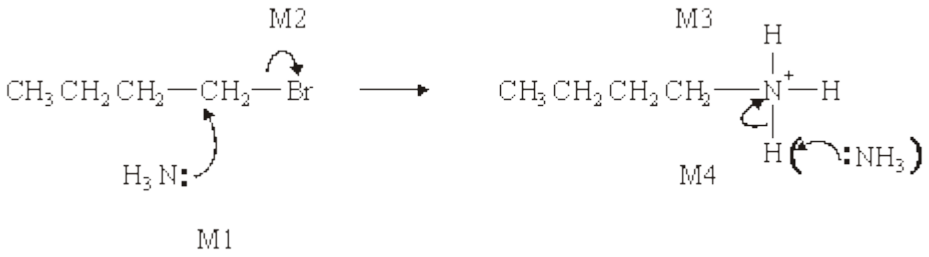
4

[15]

20 B

[1]

21 (a) Nucleophilic substitution



1

M1, M2 and M4 for arrows, M3 for structure of cation

(Allow M2 alone first, i.e. SN1 formation of carbocation)

(Penalise M4 if Br^- used to remove H^+)

4

(b) Step 1 $CH_3CH_2CH_2CN$ 1

$CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$ balanced

1

(or CN^-) (or Br^-)
(*not HCN*)

1

Step 2 $CH_3CH_2CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2CH_2NH_2$
(or 4[H])

1

(c) (i) Lone pair (on N) (in correct context)

1

R group increases electron density / donates electrons /pushes electrons / has positive inductive effect

1

(ii) Any strong acid (but not concentrated)
or any amine salt or ammonium salt of a strong acid

1

(d) $CH_3CH_2N(CH_3)_2$

1

[12]

22 B

[1]

23 (a) Cyclohexane evolves 120 kJ mol^{-1}

∴ (expect triene to evole) 360 kJ mol^{-1} **(1)** or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

*QofL: benzene lower in energy / <u>more</u> (stated) stable **(1)***
Not award if mentions energy required for bond breaking

*due to <u>delocalisation</u> **(1)** or explained*

4

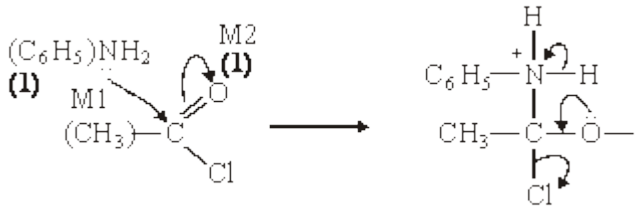
(b) (i) phenylamine weaker **(1)**

if wrong no marks

lone pair on N (less available) **(1)**
delocalised into ring **(1)** or "explained"

3

(ii) addition – elimination **(1)**



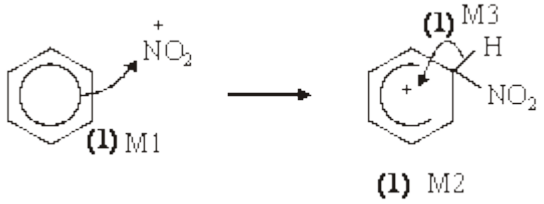
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)**
conc H_2SO_4 **(1)**

$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$ **(1)**



6

(iv) peptide / amide **(1)**

NaOH (aq) **(1)**

HCl conc or dil or neither

H_2SO_4 dil NOT conc

NOT just H_2O

2

Notes

(a)
- 360 or 3 × 120 or in words **(1)**;
- 152 NOT 150 **(1)**; (152 can get first two marks)
- **Q of L** benzene more stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene **(1)**;
- delocalisation or explained **(1)**

(b) (ii) or N-phenylacetamide or acetanilide
mechanism: if shown as substitution can only gain M1
if CH_3CO+ formed can only gain M1

lose M4 if Cl^- removes H^+
be lenient with structures for M1 and M2 but must be correct for M3

 alone loses M2

(iii) **No marks for name of mechanism in this part**
if conc missing can score one for both acids (or in equation)
allow two equations

allow $HNO_3 + H_2SO_4 \rightarrow NO^{2+} + HSO_4^- + H_2O$
ignore side chain in mechanism even if wrong
arrow for M1 must come from niside hexagon
arrow to NO_2^+ must go to N but be lenient over position of +
+ must not be too near "tetrahedral" Carbon
horseshoe from carbons 2-6 but don't be too harsh

(iv) reagent allow NaOH
HCl conc or dil or neither
H_2SO_4 dil or neither but not conc
not just H_2O

[21]

24 **X** is CH_3CN or ethanenitrile or ethanonitrile or methyl cyanide or cyanomethane or ethyl nitrile or methanecarbonitrile

Not *ethanitrile*
but contradiciton of name and structure lose marks

1

Y is $CH_3CH_2NH_2$ or ethylamine or aminoethane or ethanamine

1

Step 1: reagent KCN not HCN/HCl
condition (aq)/alcohol - only allow condition if reagent correct or incomplete

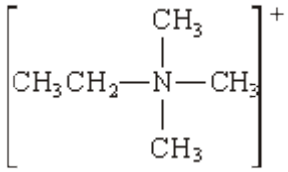
2

Step 2: reagent H_2 $LiAlH_4$ Na Zn/Fe/Sn Not $NaBH_4$
condition Ni/Pt/Pd ether ethanol HCl

2

Z is an amine or aminoalkane or named amine even if incorrect name for **Z**
secondary (only award if amine correct)

1



(Br^-) + can be on N or outside brackets as shown

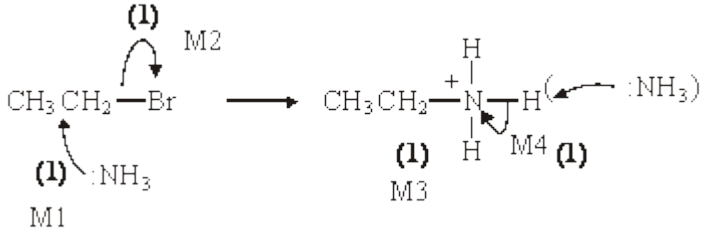
1

nucleophilic substitution

1

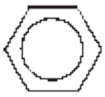
[9]

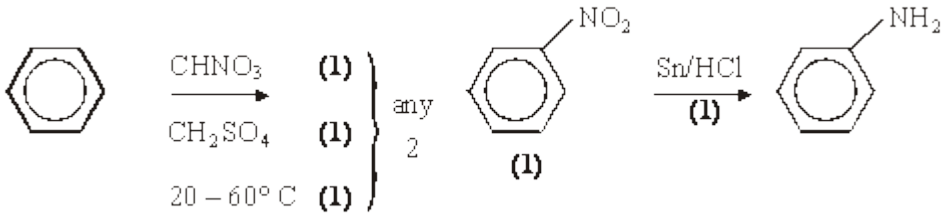
25 (a)



Further reaction / substitution / formation of 2° / 3° amines etc **(1)**
use an excess of NH_3 **(1)**

6

(b)  repels nucleophiles (such as NH_3) **(1)**



5

Notes

(a) allow S_N1
penalise: Br^- intead of NH_3 removing H^+ for M4
not contamination with *other amines* (this is in the question) not diamines

(b) allow because NH_3 is a nuclephile or benzene is (only) attacked by electrophiles
or C–Br bond (in bromobenzene) is stronger / less polar or Br lp delocalized

HNO_3 / H_2SO_4 without either conc scores **(1)** allow 20 – 60° for **(1)** (any 2 ex 3)

allow name or structure of nitrobenzene

other reducing agents: Fe or Sn with HCl (conc or dil or neither)
not conc H_2SO_4 or conc HNO_3
allow Ni/H_2
Not $NaBH_4$ or $LiAlH_4$
ignore wrong descriptions for reduction step e.g. hydrolysis or hydration

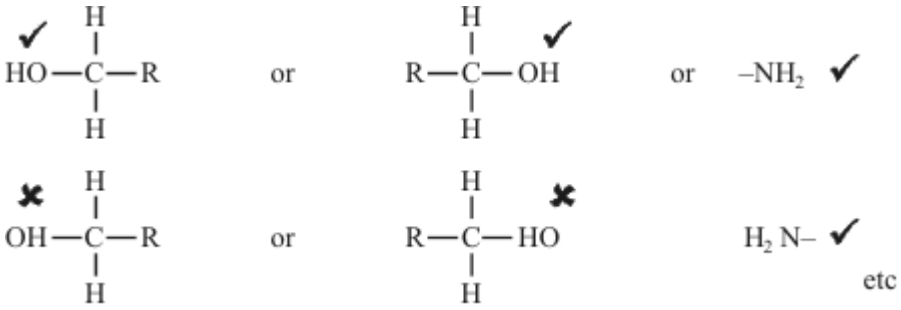
[11]

Organic points

(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.

(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH_3– or –CH_3 or  or CH_3
or H_3C–

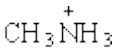
26

(a) (i) H+ or proton acceptor **(1)**

$CH_3NH_2 + H_2O$ (⇌) $CH_3^+NH_3$ (+) OH^- **(1)**

(ii) CH_3NH_3Cl or HCl **(1)**

Or any ammonium compound or strong acid name or formula

(iii) extra OH^- reacts with 
or reaction / equilibrium moves to left
or ratio salt / base remains almost constant **(1)**

Any 2

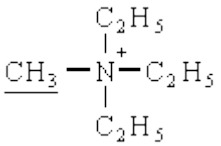
5

(b) lone pair (on N accepts H^+) **(1)**

CH_3 increases electron density (on N)
donates / pushes electrons
has positive inductive effect **(1)**

2

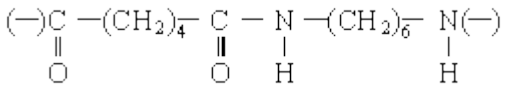
(c) nucleophilic substitution **(1)**


(1)

2

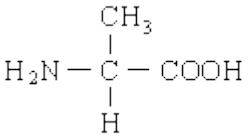
[9]

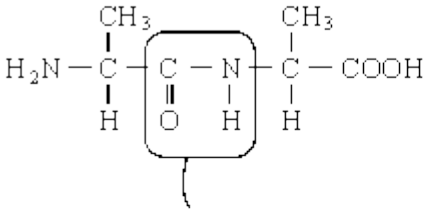
27 (a) (i) hexane-1,6-diamine or 1,6-diaminohexane **(allow ammine)** or 1,6 hexan(e)diamine **(1)**

(ii) 
(1)

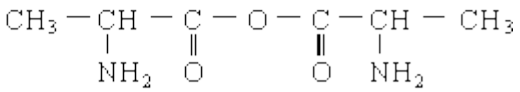
Allow –CONH–

2

(b) (i) 
(1)

(ii) 
(1)

peptide link essential : the rest is consequential on b(i)
(allow CONH)

allow anhydride 

2

(c) (i) quaternary ammonium bromide salt **(1)**

(not ion, not compound)

Allow quarternery

(ii) *Reagent*: CH_3Br or bromomethane **(1)**

penalise CH_3Cl but allow excess for any halomethane

Condition: excess (CH_3Br) **(1)**

(iii) nucleophilic substitution **(1)**

4

[8]