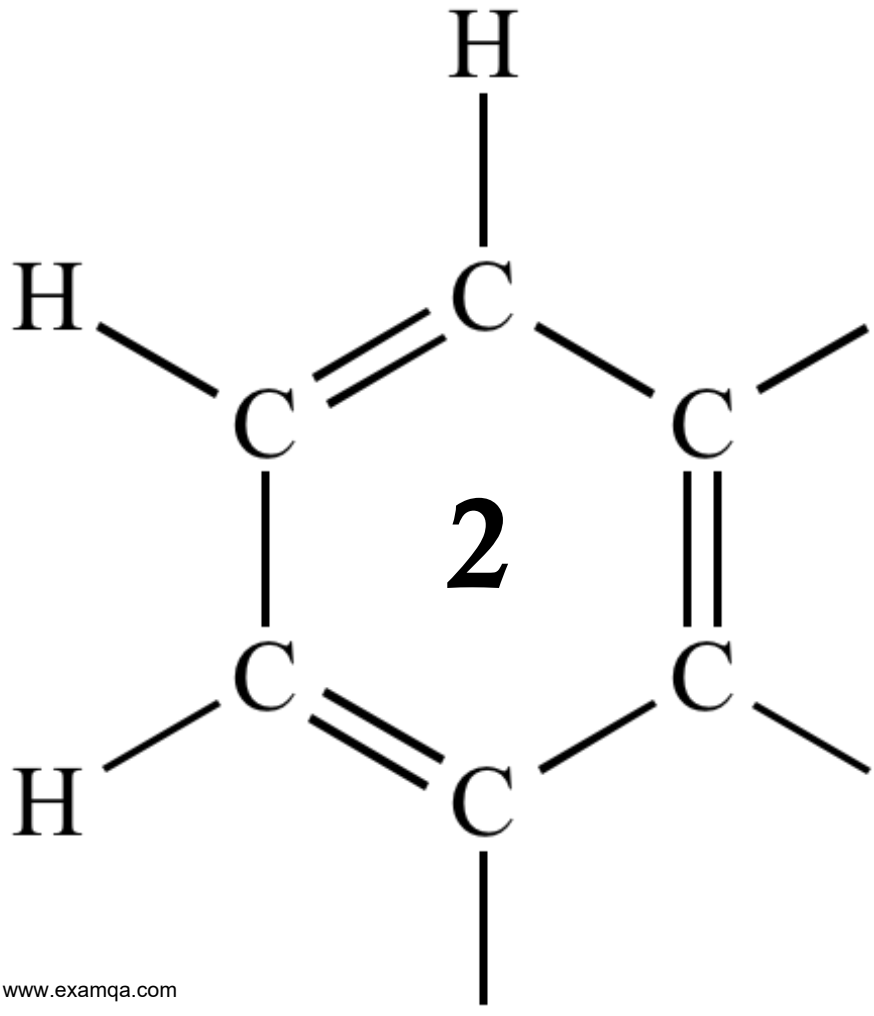
LONDON SCIENCE COLLEGE

OCR A2 CHEMISTRY

MODULE 6.2

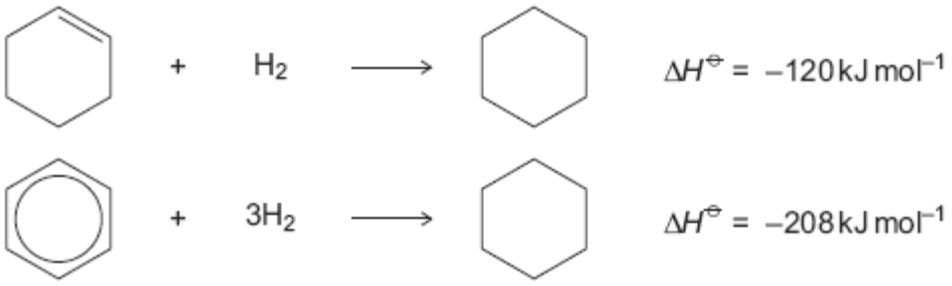
NITROGEN COMPOUNDS

POLYMERS



1 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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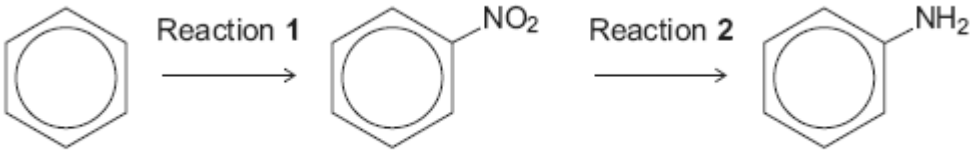
(4)

(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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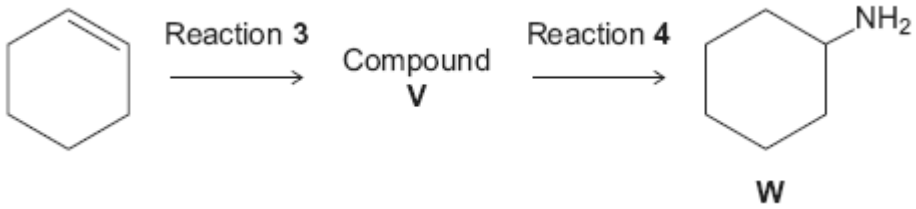
(6)

(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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(6)

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

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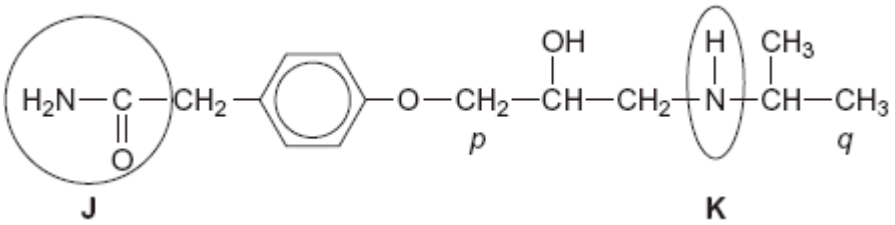
(3)
(Total 19 marks)

2 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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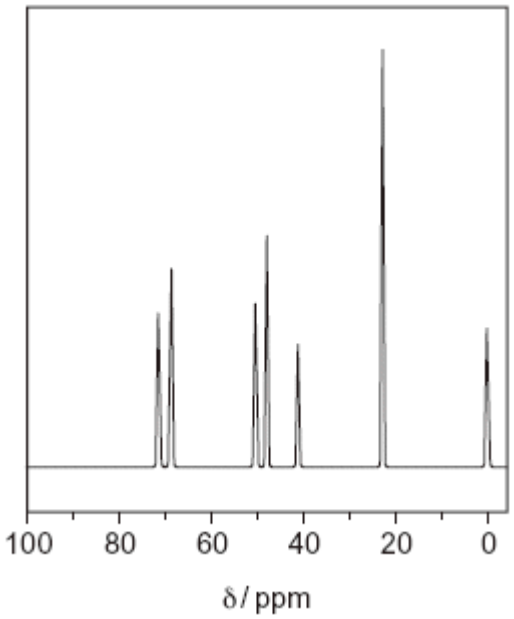
(1)

(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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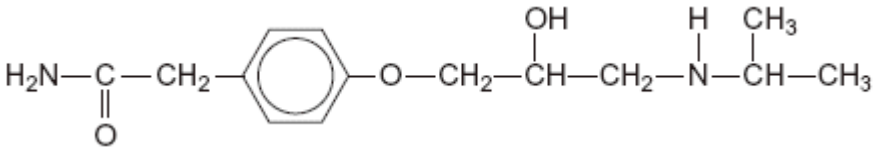
(1)

(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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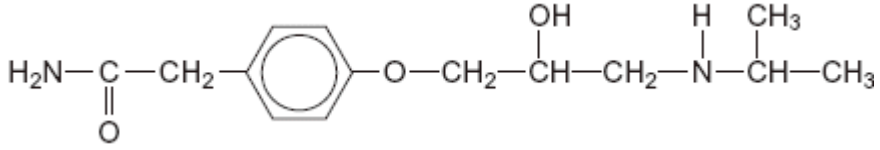
(1)

(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 .....

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Disadvantage .....

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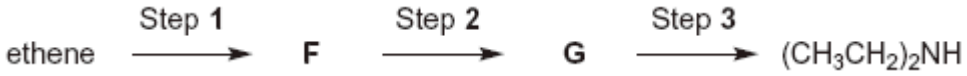
(2)
(Total 16 marks)

3 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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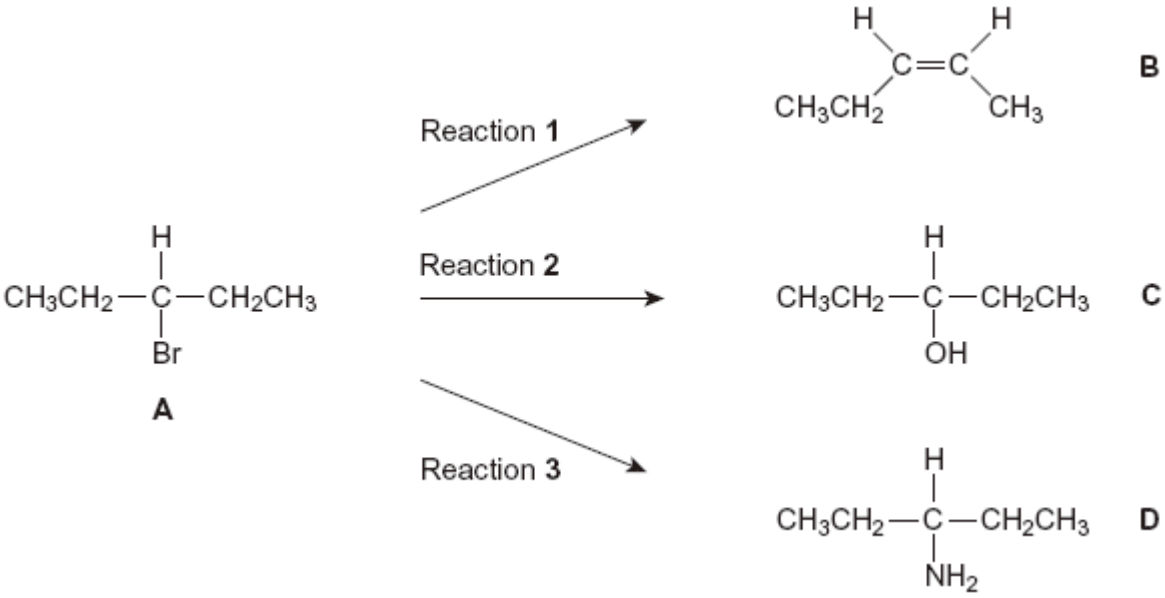
(2)
(Total 11 marks)

4 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**.

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(1)

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

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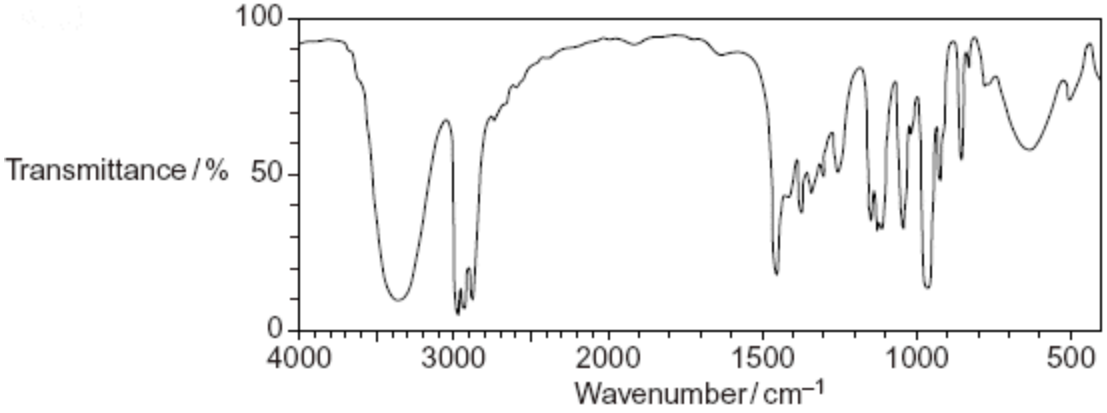
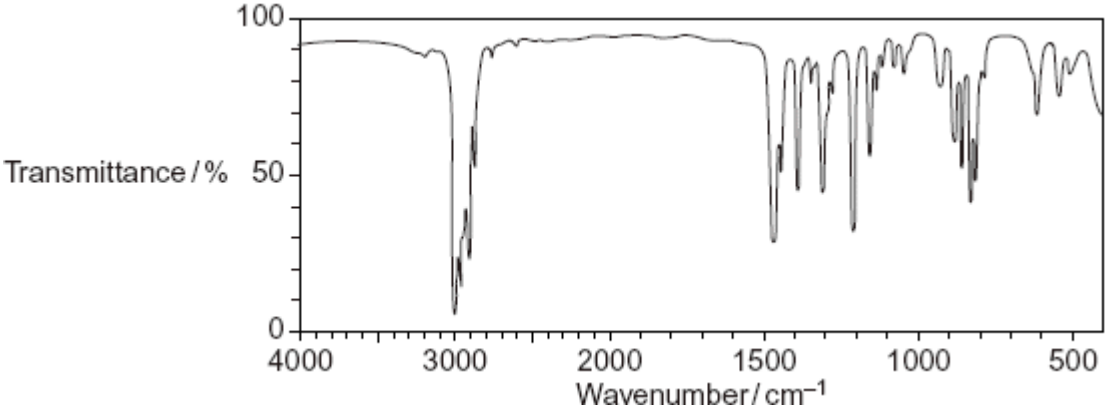
(1)

(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.

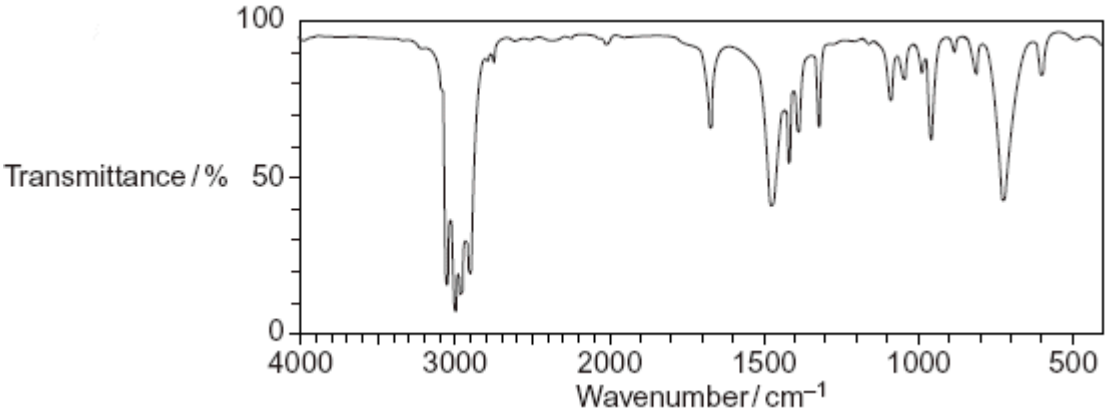
(i)



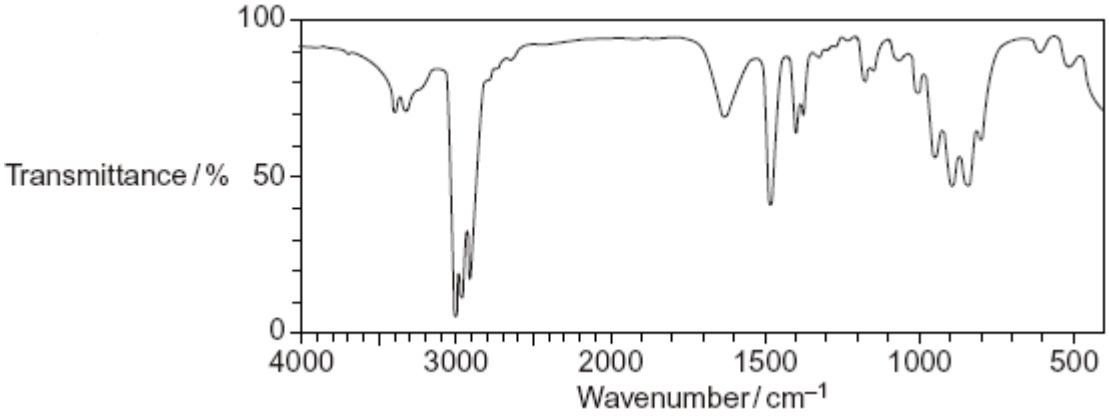
(ii)



(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.

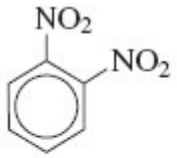
(i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1)

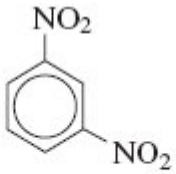
(ii) Another isomer of **D** is a tertiary amine. Its ^{1}H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

(1)
(Total 17 marks)

5 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)

6 (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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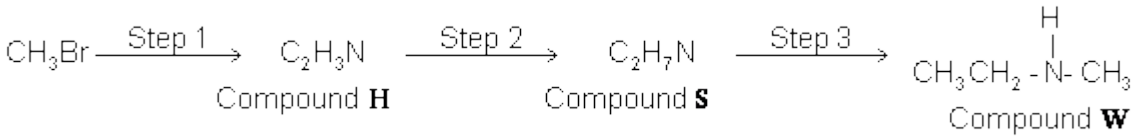
(6)
(Total 12 marks)

7 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)

8 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)