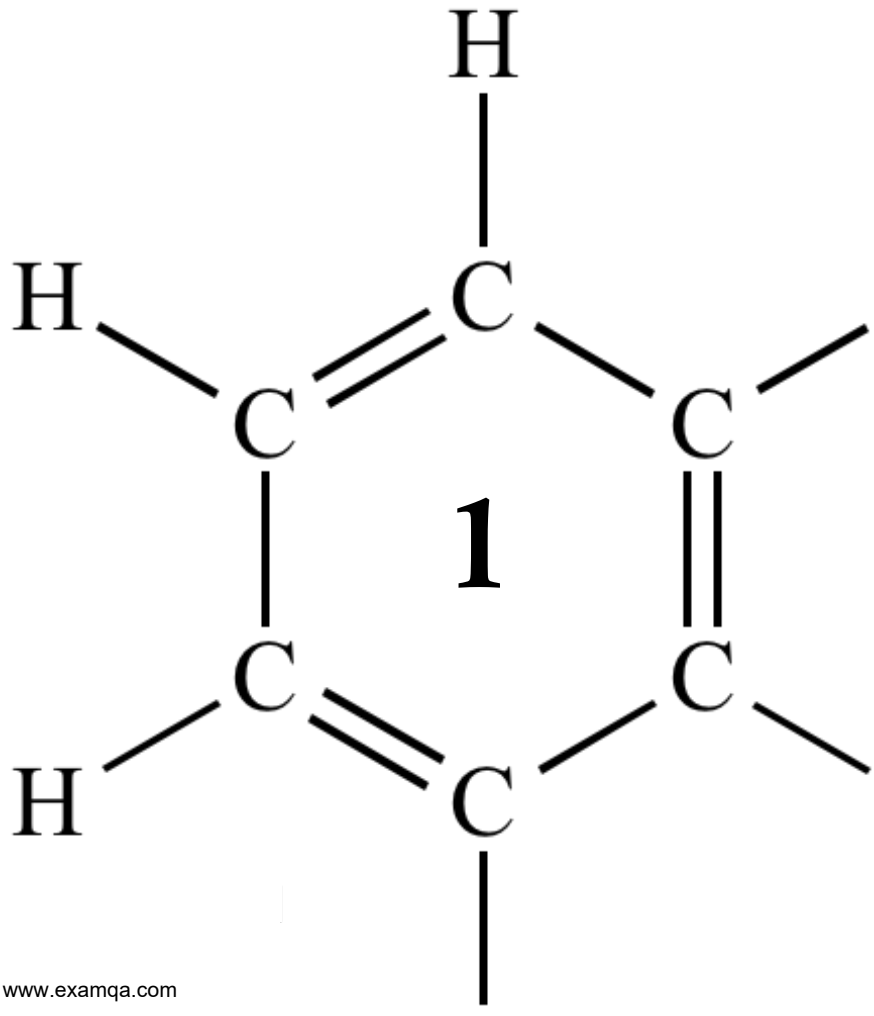
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

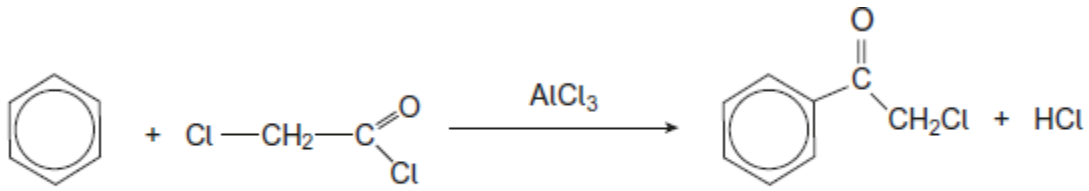
AROMATIC ~ AMINES

AROMATIC



1 Compound **X** ($ClCH_2COCl$) is used as a reagent in organic synthesis.

(a) One important reaction of **X** is in the preparation of compound **P** as shown.



X **P**

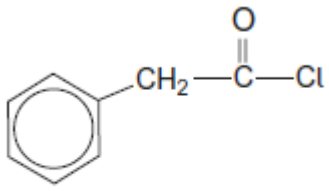
(i) Draw the structure of the electrophile formed by the reaction of **X** with $AlCl_3$.

(1)

(ii) Outline the mechanism for the reaction of the electrophile from part **(a)(i)** with benzene in the preparation of **P**.

(3)

(b) Compound **Q** is an alternative product that could be formed when **X** reacts with benzene.



Q

Describe how you could distinguish between **P** and **Q** by a test-tube reaction.
Give the reagent used and the observation with each compound.

Reagent .....

Observation with **P** .....

Observation with **Q** .....

(3)

(c) **X** is also used to make the compound $HOCH_2COOH$. This compound is polymerised to form the polymer known as PGA. PGA is used in surgical sutures (stitches).

(i) Draw the repeating unit of PGA.

(1)

(ii) Production of PGA occurs via a cyclic compound. Two $HOCH_2COOH$ molecules react together to form the cyclic compound and two molecules of water.

Draw the structure of this cyclic compound.

(1)

(d) Poly(propene) is also used in surgical sutures.

(i) Draw the repeating unit of poly(propene).

(1)

(ii) Suggest an advantage of surgical sutures made from PGA rather than from poly(propene).
Explain your answer.

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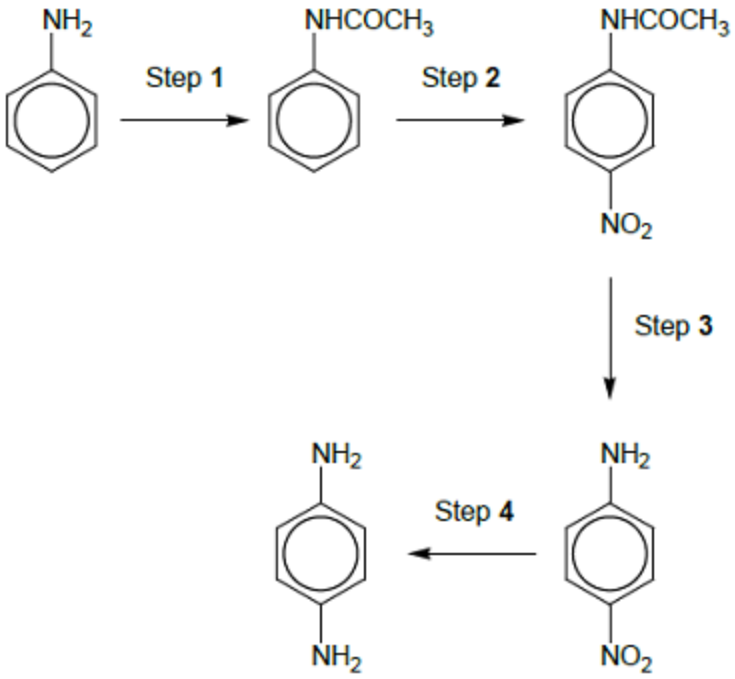
(2)
(Total 12 marks)

2 1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

A possible synthesis of 1,4-diaminobenzene from phenylamine is shown in the following figure.



(a) A suitable reagent for step **1** is CH_3COCl

Name and draw a mechanism for the reaction in step **1**.

Name of mechanism .....

Mechanism

(5)

(b) The product of step **1** was purified by recrystallisation as follows.

The crude product was dissolved in **the minimum quantity of hot water** and the hot solution was filtered through a hot filter funnel into a conical flask. This filtration removed any insoluble impurities. The flask was **left to cool to room temperature**.
The crystals formed were filtered off using a Buchner funnel and a clean cork was used **to compress the crystals in the funnel. A little cold water was then poured through the crystals.**
After a few minutes, the crystals were removed from the funnel and weighed.
A small sample was then used to find the melting point.

Give reasons for each of the following practical steps.

The minimum quantity of hot water was used

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The flask was cooled to room temperature before the crystals were filtered off

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The crystals were compressed in the funnel

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A little cold water was poured through the crystals

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(4)

(c) The melting point of the sample in part (b) was found to be slightly lower than a data-book value.

Suggest the most likely impurity to have caused this low value and an improvement to the method so that a more accurate value for the melting point would be obtained.

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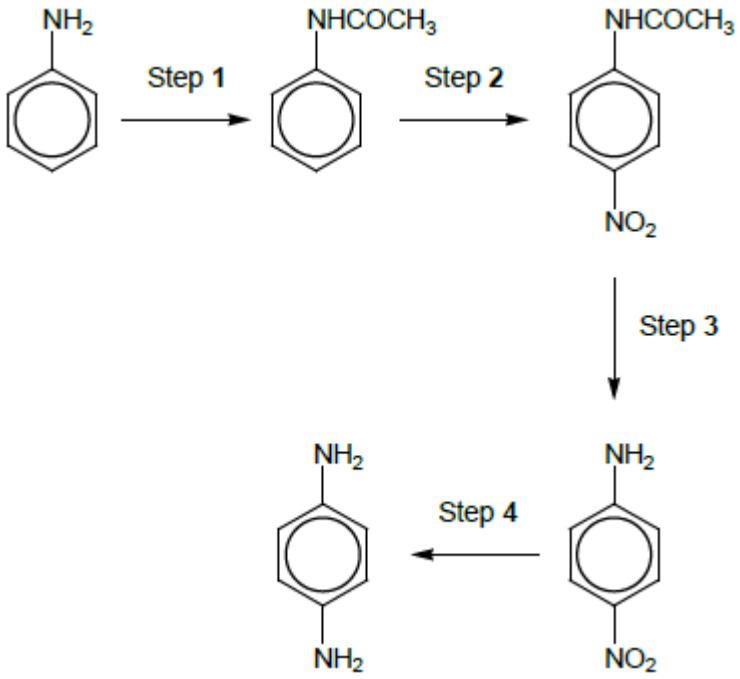
(2)

The figure above is repeated here to help you answer the following questions.



(d) In an experiment starting with 5.05 g of phenylamine, 4.82 g of purified product were obtained in step **1**.

Calculate the percentage yield in this reaction.
Give your answer to the appropriate number of significant figures.

Percentage yield = ...%

(3)

(e) A reagent for step **2** is a mixture of concentrated nitric acid and concentrated sulfuric acid, which react together to form a reactive intermediate.

Write an equation for the reaction of this intermediate in step **2**.

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(1)

(f) Name a mechanism for the reaction in step **2**.

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(1)

(g) Suggest the type of reaction occurring in step **3**.

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(1)

(h) Identify the reagents used in step **4**.

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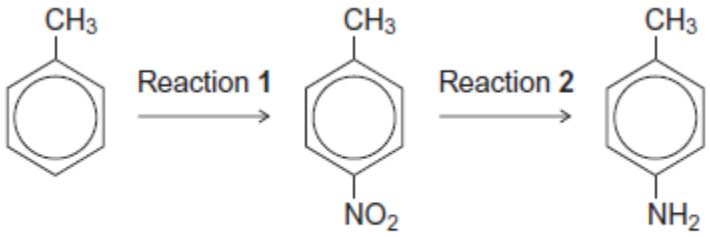
(1)

(Total 18 marks)

3 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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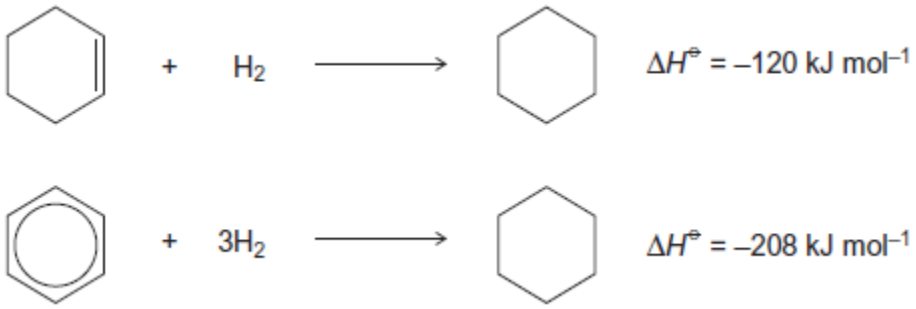
(3)
(Total 11 marks)

4 Equations for the hydrogenation of cyclohexene and of benzene, together with the enthalpies of hydrogenation, are shown.



(a) (i) Use these data to show that benzene is 152 kJ mol^{-1} more stable than the hypothetical compound cyclohexa−1,3,5−triene.

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(1)

(ii) State, in terms of its bonding, why benzene is more stable than cyclohexa−1,3,5−triene.

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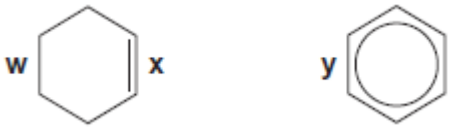
(1)

(b) Three carbon−carbon bonds are labelled on the structures shown.
These bonds are of different lengths.



Write the letters **w**, **x** and **y** in order of **increasing** bond length.

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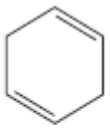
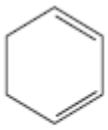
(1)

(c) The structures of two cyclic dienes are shown.



cyclohexa-1,4-diene



cyclohexa-1,3-diene

(i) Use the enthalpy of hydrogenation data given opposite to calculate a value for the enthalpy of hydrogenation of cyclohexa−1,4−diene.

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(1)

(ii) Predict a value for the enthalpy of hydrogenation of cyclohexa−1,3−diene.

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(1)

(iii) Explain your answers to part (i) and part (ii) in terms of the bonding in these two dienes.

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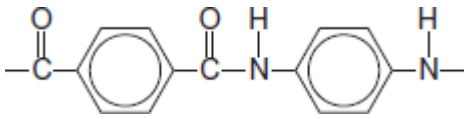
(3)
(Total 8 marks)

5 Kevlar is a polymer used in protective clothing.
The repeating unit within the polymer chains of Kevlar is shown.



(a) Name the strongest type of interaction between polymer chains of Kevlar.

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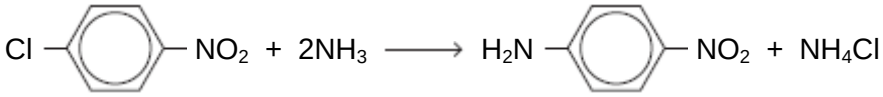
(1)

(b) One of the monomers used in the synthesis of Kevlar is

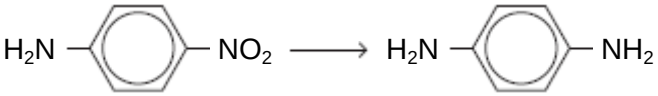
An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**



X

Stage **2**



(i) Suggest why the reaction of ammonia with **X** in Stage **1** might be considered unexpected.

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(2)

(ii) Suggest a combination of reagents for the reaction in Stage **2**.

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(1)

(iii) Compound **X** can be produced by nitration of chlorobenzene.

Give the combination of reagents for this nitration of chlorobenzene.
Write an equation or equations to show the formation of a reactive intermediate from these reagents.

Reagents .....

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Equation(s) .....

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(3)

(iv) Name and outline a mechanism for the formation of **X** from chlorobenzene and the reactive intermediate in part (iii).

Name of mechanism .....

Mechanism

(4)
(Total 11 marks)

6 This question is about acylium ions, $[RCO]^+$

(a) The acylium ion $H_3C-\overset{+}{C}=O$ is formed in a mass spectrometer by fragmentation of the molecular ion of methyl ethanoate.

Write an equation for this fragmentation.

Include in your answer a displayed formula for the radical formed.

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(2)

(b) The acylium ion $H_3C-\overset{+}{C}=O$ can also be formed from ethanoyl chloride. The ion reacts with benzene to form $C_6H_5COCH_3$

(i) Write an equation to show the formation of this acylium ion by the reaction of ethanoyl chloride with **one** other substance.

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(2)

(ii) Name and outline a mechanism for the reaction of benzene with this acylium ion.

Name of mechanism .....

Mechanism

(4)

(iii) Ethanoic anhydride also reacts with benzene to form $C_6H_5COCH_3$

Write an equation for this reaction.

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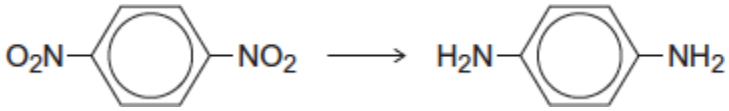
(1)

(Total 9 marks)

7 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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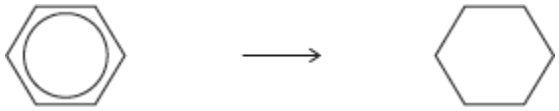
(5)

(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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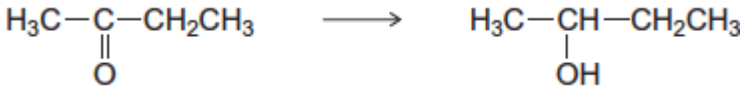
(4)

(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)