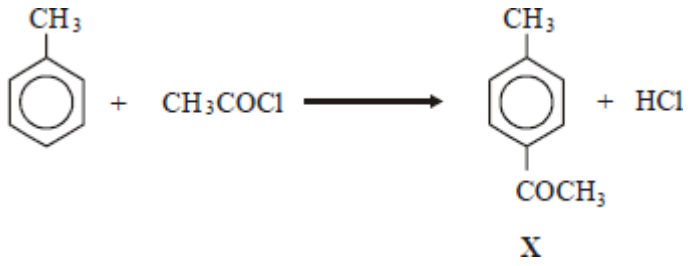
Q1. Ethanoyl chloride reacts with methylbenzene forming compound **X** according to the equation below.



X

If the experimental yield is 40.0%, the mass in grams of **X** (M_r = 134.0) formed from 18.4 g of methylbenzene (M_r = 92.0) is

A 26.8

B 16.1

C 10.7

D 7.4

(Total 1 mark)

Q2. In a reaction which gave a 27.0% yield, 5.00 g of methylbenzene were converted into the explosive 2,4,6-trinitromethylbenzene (TNT) (M_r = 227.0). The mass of TNT formed was

A 1.35 g

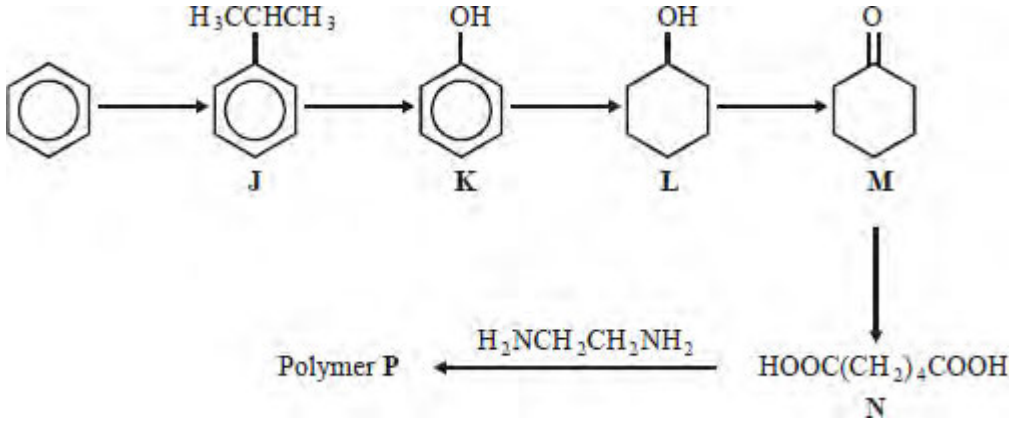
B 3.33 g

C 3.65 g

D 12.34 g

(Total 1 mark)

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



If 1.0 kg of benzene gave 0.98 kg of **J**, the percentage yield of **J** was

A 64

B 66

C 68

D 70

(Total 1 mark)

Q4. In which one of the following reactions is the role of the reagent stated correctly?

	Reaction	**Role of reagent**
A	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$	TiO_2 is an oxidising agent
B	$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$	HNO_3 is a Brønsted-Lowry acid
C	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	$AlCl_3$ is a Lewis base
D	$2CO + 2NO \rightarrow 2CO_2 + N_2$	CO is a reducing agent

(Total 1 mark)

Q5. The relative molecular mass (M_r) of benzene-1,4-dicarboxylic acid is

A 164

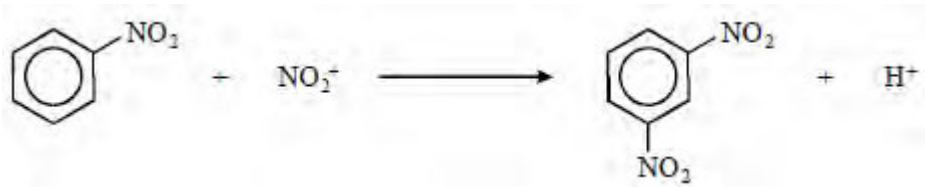
B 166

C 168

C 170

(Total 1 mark)

Q6.1,3-dinitrobenzene can be prepared by heating nitrobenzene with a mixture of fuming nitric acid and concentrated sulphuric acid. The reaction can be represented by the following equation.



If the yield of the reaction is 55%, the mass of 1,3-dinitrobenzene produced from 12.30 g of nitrobenzene is

A 16.90 g

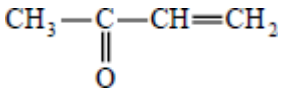
B 16.80 g

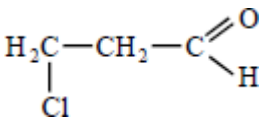
C 9.30 g

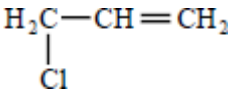
D 9.24 g

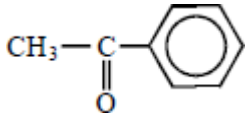
(Total 1 mark)

Q7. Which one of the following can react both by nucleophilic addition and by nucleophilic substitution?

A 

B 

C 

D 

(Total 1 mark)

Q8. Which one of the following does **not** contain any delocalised electrons?

A poly(propene)

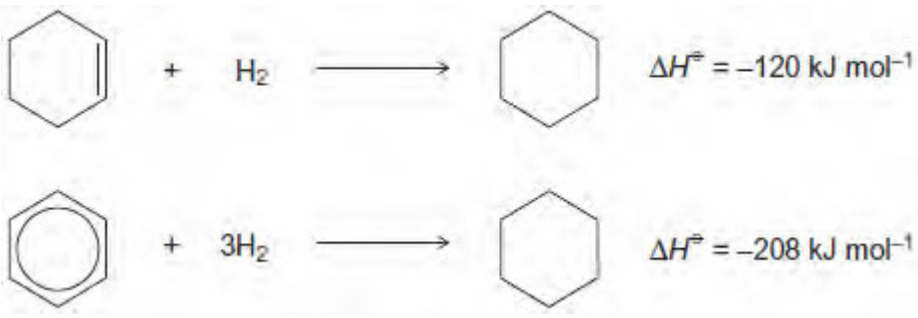
B benzene

C graphite

D sodium

(Total 1 mark)

Q1. 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.

.....

.....

.....

.....

(1)

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

.....

.....

.....

.....

(1)

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

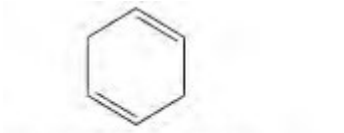


Write the letters **w**, **x** and **y** in order of **increasing** bond length.

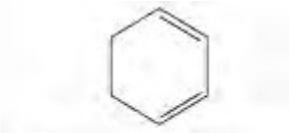
.....

(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.

.....

.....

(1)

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

.....

(1)

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

.....

.....

.....

.....

.....

.....

(3)
(Total 8 marks)

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

(a) Consider the following conversion.



Identify a reducing agent for this conversion.

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

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

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

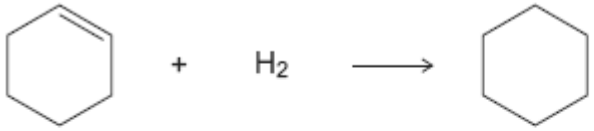
.....

.....

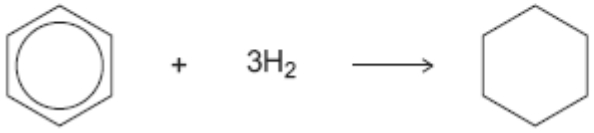
(3)
(Total 17 marks)

Q3. 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.



$\Delta H^{\ominus} = -120\,kJ\,mol^{-1}$



$\Delta H^{\ominus} = -208\,kJ\,mol^{-1}$

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

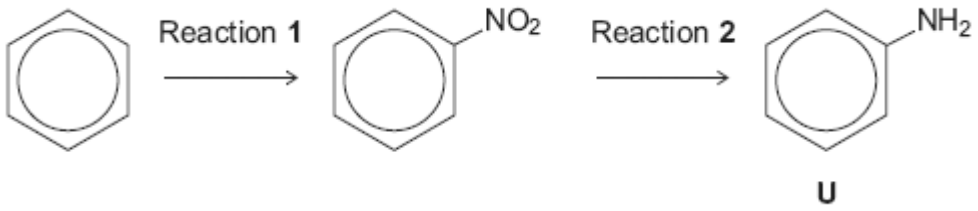
.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

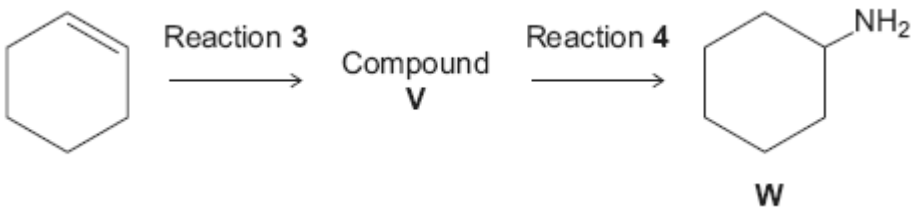
.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

(6)

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

.....

.....

.....

.....

.....

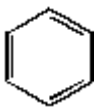
(Extra space) .....

.....

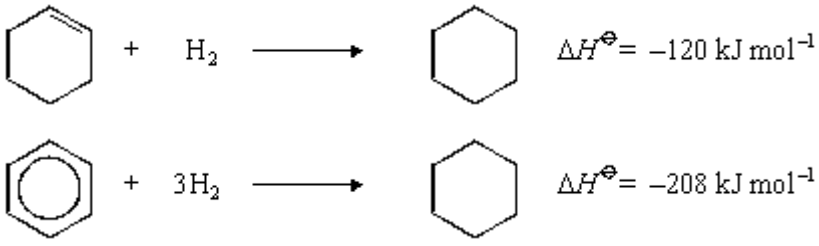
.....

(3)
(Total 19 marks)

Q1. (a) Use the following data to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.

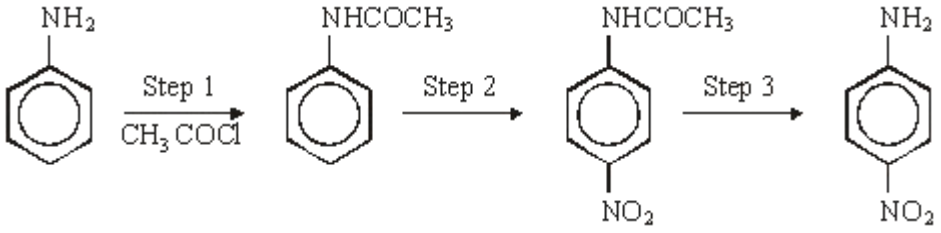


Give a reason for this difference in stability.



(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)

Q2. Which one of the following does **not** contain any delocalised electrons?

A poly(propene)

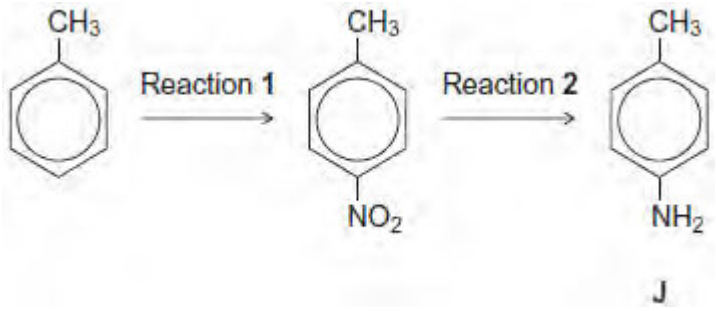
B benzene

C graphite

D sodium

(Total 1 mark)

Q1. Consider the following reaction sequence starting from methylbenzene.



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

.....

(1)

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

(i) Give a reducing agent for this reaction.

.....

(1)

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

.....

(1)

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

.....

(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**.

.....

.....

.....

.....

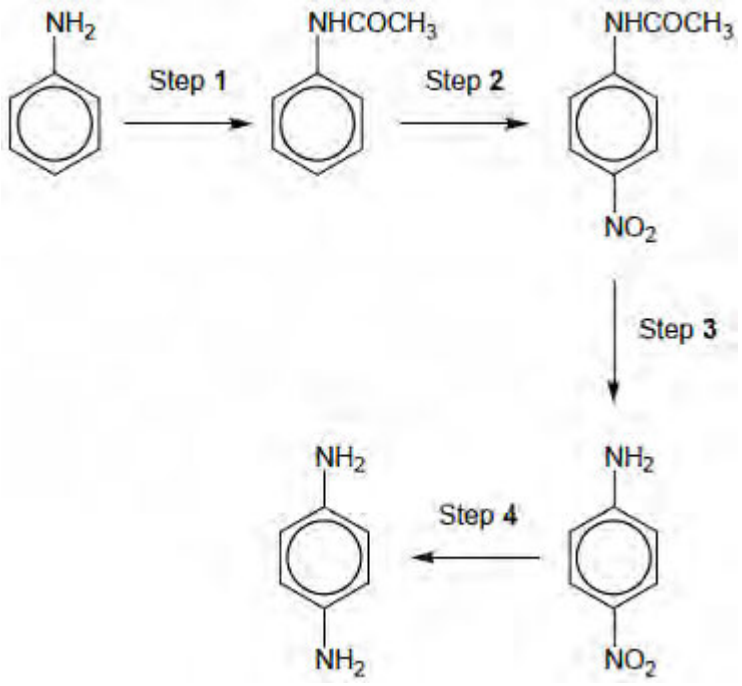
.....

.....

(3)
(Total 11 marks)

Q2. 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

.....

.....

.....

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

.....

.....

.....

The crystals were compressed in the funnel

.....

.....

.....

A little cold water was poured through the crystals

.....

.....

.....

(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.

.....

.....

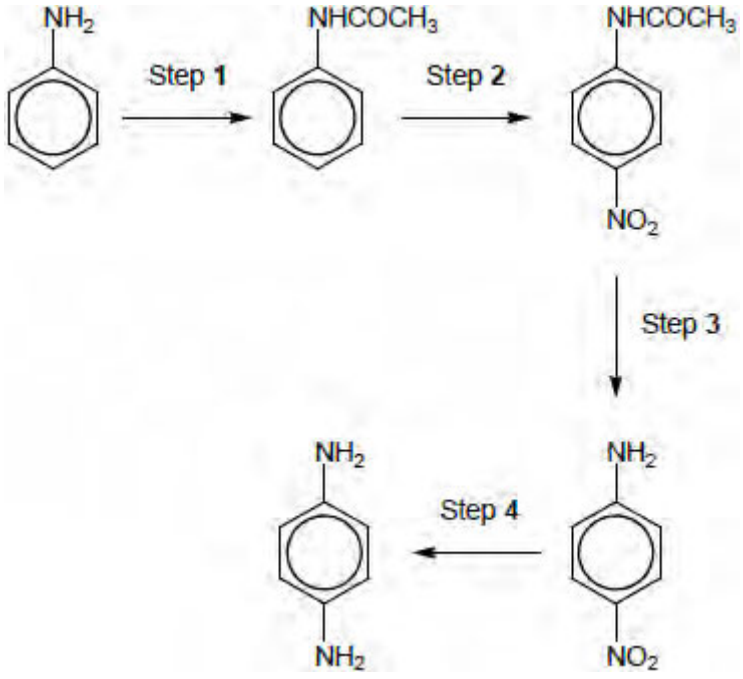
.....

.....

.....

(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**.

.....

(1)

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

.....

(1)

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

.....

(1)

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

.....

(1)

(Total 18 marks)

Q3. Benzene reacts with ethanoyl chloride in a substitution reaction to form $C_6H_5COCH_3$. This reaction is catalysed by aluminium chloride.

(a) Write equations to show the role of aluminium chloride as a catalyst in this reaction.

Outline a mechanism for the reaction of benzene.

Name the product, $C_6H_5COCH_3$.

.....

.....

.....

(6)

(b) The product of the substitution reaction ($C_6H_5COCH_3$) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with *m/z* = 105.
Draw the structure of this fragment ion.

(1)

(c) When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene.
Suggest why the reaction of methylbenzene is faster.

.....

.....

.....

.....

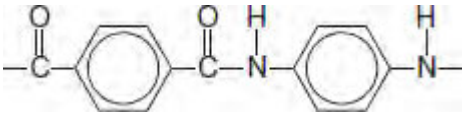
.....

.....

(2)
(Total 9 marks)

Q4. 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.

.....

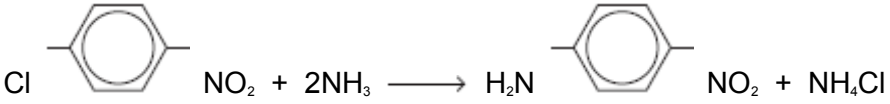
(1)

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



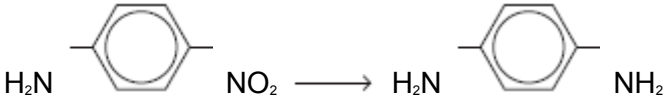
An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**



X

Stage **2**



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

.....

.....

.....

.....

(2)

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

.....

(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 .....

.....

Equation(s) .....

.....

(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)

Q5. This question is about acylium ions, $[RCO]^+$

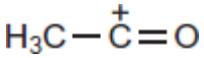
(a) The acylium ion $H_3C-\overset{+}{C}=O$ is formed in a mass spectrometer by fragmentation of the molecular ion of methyl ethanoate.

Write an equation for this fragmentation.

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

.....

(2)

(b) The acylium ion  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.

.....

(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 $C_6H_5COCH_3$

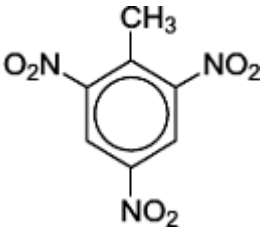
Write an equation for this reaction.

.....

(1)

(Total 9 marks)

Q1. Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



(a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.

(i) Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents .....

.....

Equation .....

.....

(3)

(ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3)

(b) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TNT.

.....

(1)

(C) Deduce the number of peaks in the ^1H n.m.r. spectrum of TNT.

.....

(1)

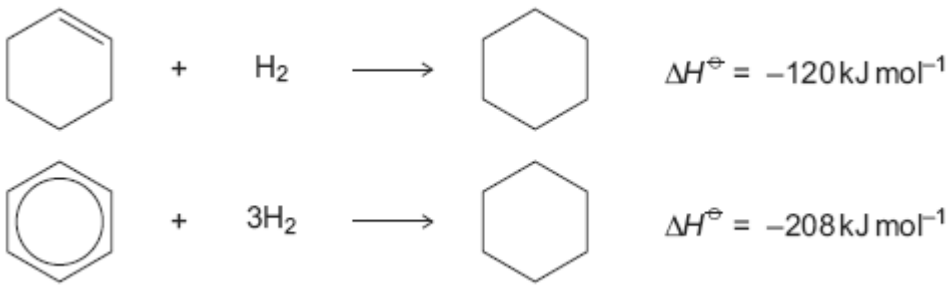
(d) Using the molecular formula ($C_7H_5N_3O_6$), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

.....

(1)
(Total 9 marks)

Q2. 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.



.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

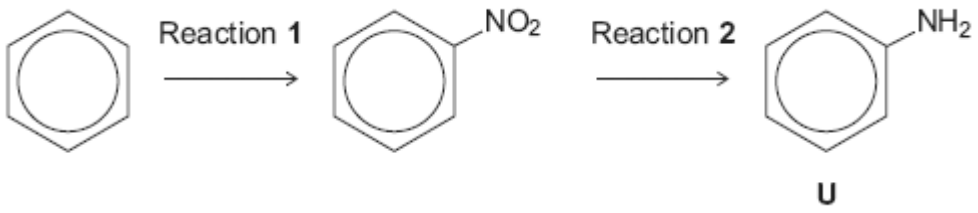
.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

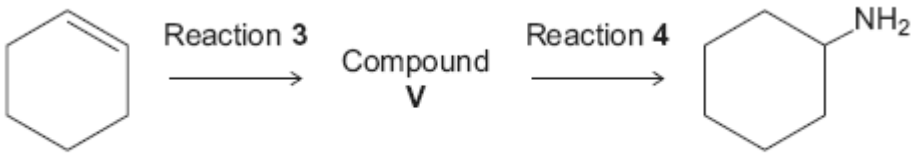
.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

(6)

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

.....

.....

.....

.....

.....

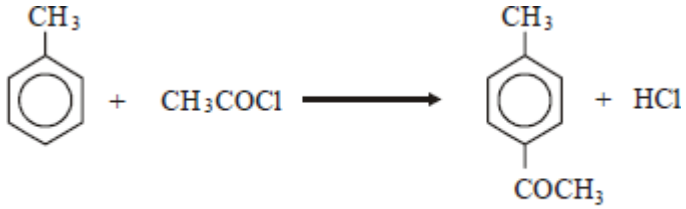
(Extra space) .....

.....

.....

(3)
(Total 19 marks)

Q3. Ethanoyl chloride reacts with methylbenzene forming compound **X** according to the equation below.



X

If the experimental yield is 40.0%, the mass in grams of **X** (M_r = 134.0) formed from 18.4 g of methylbenzene (M_r = 92.0) is

A 26.8

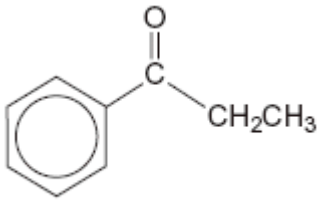
B 16.1

C 10.7

D 7.4

(Total 1 mark)

Q4. Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.



P

(a) Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

.....

.....

.....

.....

.....

.....

(3)

(b) Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

(3)

(c) Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

.....

.....

.....

.....

.....

.....

(2)
(Total 8 marks)

Q5. Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

(a) Consider the reaction of benzene with CH_3CH_2COCl

(i) Write an equation for this reaction and name the organic product.
Identify the catalyst required in this reaction.
Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

.....

.....

.....

.....

.....

.....

.....

.....

(5)

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

.....

.....

.....

.....

.....

.....

.....

.....

(4)

(b) Consider the reaction of propanal with HCN

(i) Write an equation for the reaction of propanal with HCN and name the product.

.....

.....

.....

(2)

(ii) Name and outline a mechanism for the reaction of propanal with HCN

.....

.....

.....

.....

.....

.....

.....

.....

(5)

(iii) The rate-determining step in the mechanism in part (b) (ii) involves attack by the nucleophile.
Suggest how the rate of reaction of propanone with HCN would compare with the rate of reaction of propanal with HCN
Explain your answer.

.....

.....

.....

.....

.....

.....

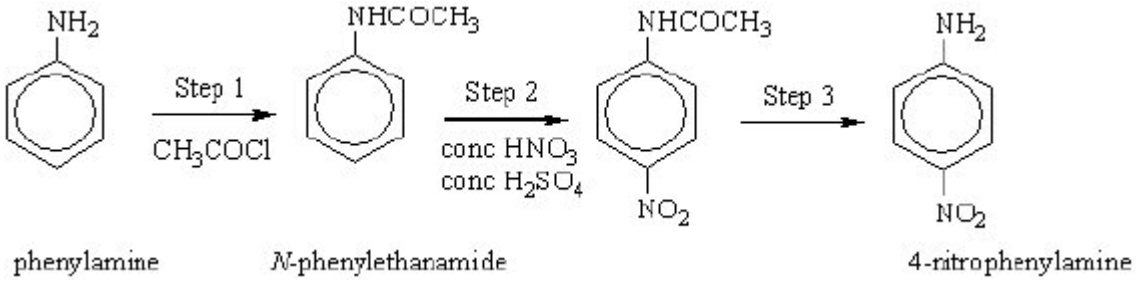
.....

.....

(2)
(Total 18 marks)

Q1. Synthetic dyes can be manufactured starting from compounds such as 4-nitrophenylamine.

A synthesis of 4-nitrophenylamine starting from phenylamine is shown below.



(a) An equation for formation of *N*-phenylethanamide in Step 1 of the synthesis is shown below.

$$2C_6H_5NH_2 + CH_3COCl \rightarrow \underset{\text{N-phenylethanamide}}{C_6H_5NHCOCH_3} + C_6H_5NH_3Cl$$

(i) Calculate the % atom economy for the production of *N*-phenylethanamide (M_r = 135.0).

(ii) In a process where 10.0 kg of phenylamine are used, the yield of *N*-phenylethanamide obtained is 5.38 kg.

Calculate the percentage yield of *N*-phenylethanamide.

(iii) Comment on your answers to parts (i) and (ii) with reference to the commercial viability of the process.

(7)

(b) Name and outline a mechanism for the reaction in Step 1.

(5)

(c) The mechanism of Step 2 involves attack by an electrophile. Write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

(4)

(Total 16 marks)

Q2. In which one of the following reactions is the role of the reagent stated correctly?

	Reaction	Role of reagent
A	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$	TiO_2 is an oxidising agent
B	$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$	HNO_3 is a Brønsted-Lowry acid
C	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	$AlCl_3$ is a Lewis base
D	$2CO + 2NO \rightarrow 2CO_2 + N_2$	CO is a reducing agent

(Total 1 mark)

Q3. In a reaction which gave a 27.0% yield, 5.00 g of methylbenzene were converted into the explosive 2,4,6-trinitromethylbenzene (TNT) (M_r = 227.0). The mass of TNT formed was

A 1.35 g

B 3.33 g

C 3.65 g

D 12.34 g

(Total 1 mark)

Q4. (a) Name and outline a mechanism for the reaction between propanoyl chloride, CH_3CH_2COCl, and methylamine, CH_3NH_2
Draw the structure of the organic product.

(6)

(b) Benzene reacts with propanoyl chloride in the presence of aluminium chloride.
Write equations to show the role of aluminium chloride as a catalyst in this reaction.
Outline a mechanism for this reaction of benzene.

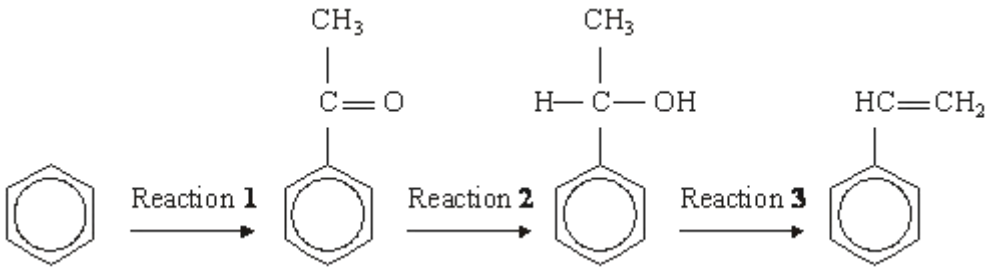
(5)

(c) Write an equation for the reaction of propanoyl chloride with water. An excess of water is added to 1.48 g of propanoyl chloride. Aqueous sodium hydroxide is then

added from a burette to the resulting solution.
Calculate the volume of 0.42 mol dm^{-3} aqueous sodium hydroxide needed to react exactly with the mixture formed.

(5)
(Total 16 marks)

Q5. A possible synthesis of phenylethene *(styrene)* is outlined below.



(a) In Reaction **1**, ethanoyl chloride and aluminium chloride are used to form a reactive species which then reacts with benzene.
Write an equation to show the formation of the reactive species.
Name and outline the mechanism by which this reactive species reacts with benzene.

(6)

(b) $NaBH_4$ is a possible reagent for Reaction **2**.
Name and outline the mechanism for the reaction with $NaBH_4$ in Reaction **2**.
Name the product of Reaction **2**.

(6)

(c) Name the type of reaction involved in Reaction **3** and give a reagent for the reaction.

(2)
(Total 14 marks)