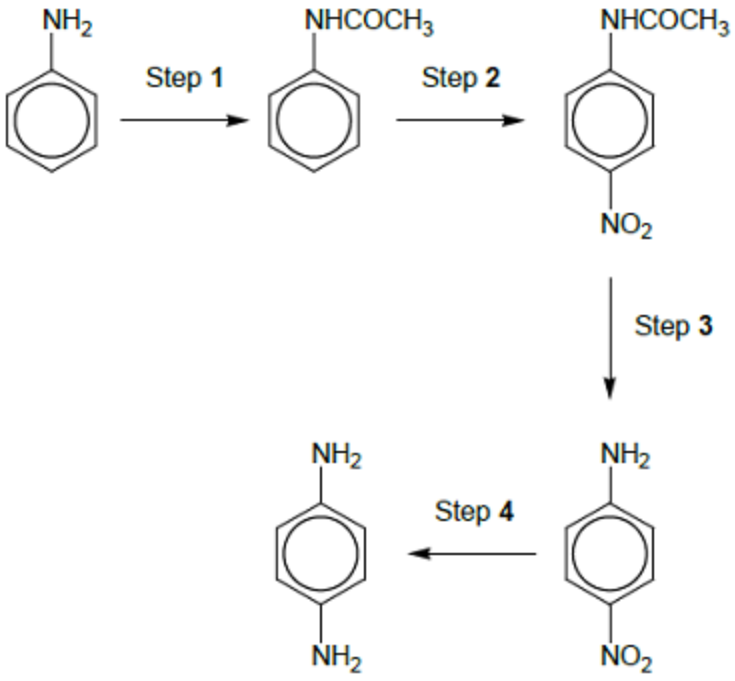
1 1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

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

.....

.....

.....

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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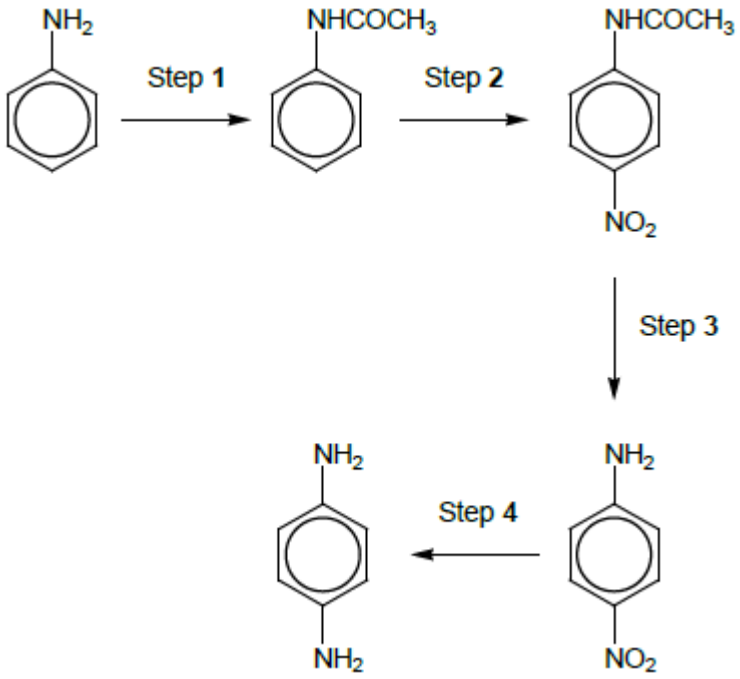
(2)

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**.

.....

(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**.

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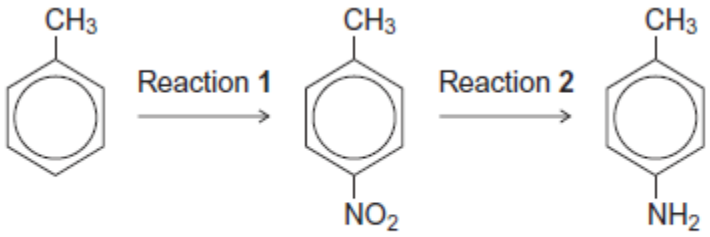
(1)

(Total 18 marks)

2 Consider the following reaction sequence starting from methylbenzene.



J

(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**.

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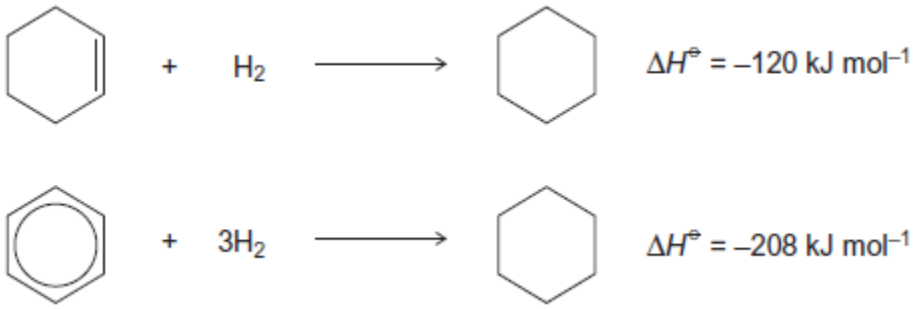
(3)
(Total 11 marks)

3 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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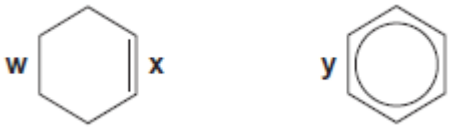
(1)

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

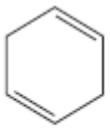


Write the letters **w**, **x** and **y** in order of **increasing** bond length.

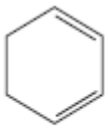
.....

(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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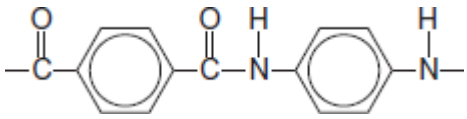
(3)
(Total 8 marks)

4 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.

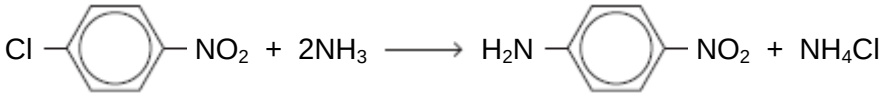
.....

(1)

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

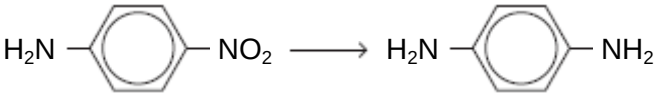
An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**



X

Stage **2**



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

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(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)

5 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 $H_3C-\overset{+}{C}=O$ 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.

.....

(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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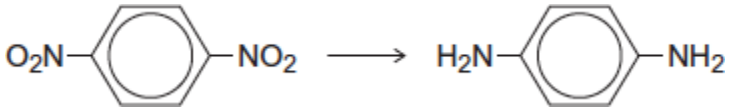
(1)

(Total 9 marks)

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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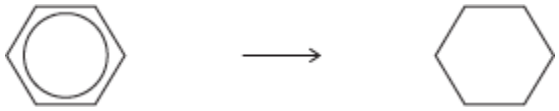
(5)

(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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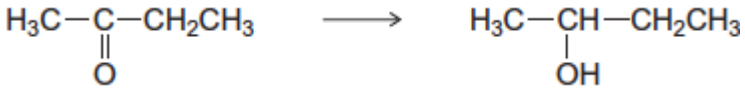
(4)

(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 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, $C_6H_5COCH_3$.

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(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.

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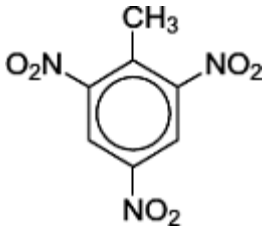
(2)
(Total 9 marks)

8 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.

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(1)

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

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(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.

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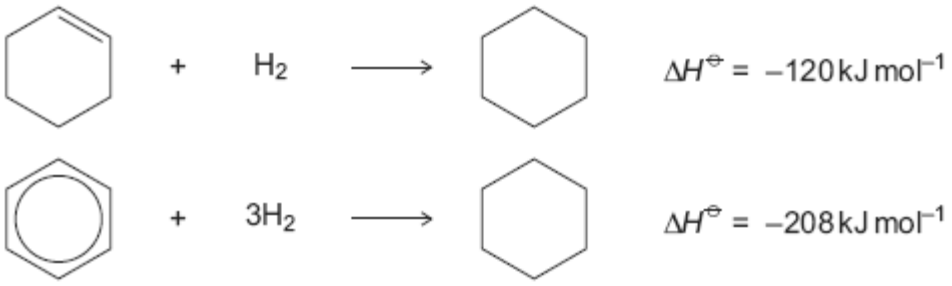
(1)
(Total 9 marks)

9 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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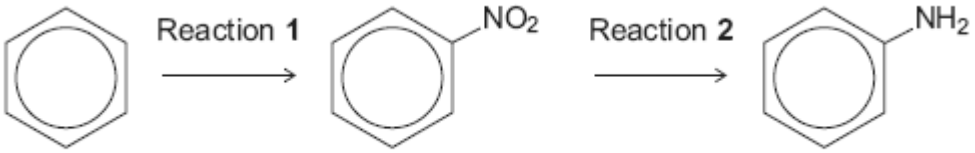
(4)

(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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(Extra space) .....

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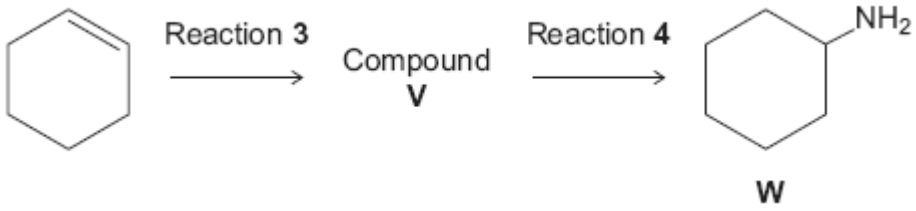
(6)

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



Suggest an identity for compound **V**.

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

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

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

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(Extra space) .....

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(6)

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

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(Extra space) .....

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(3)
(Total 19 marks)

10 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.

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(5)

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

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(4)

(b) Consider the reaction of propanal with HCN

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

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(2)

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

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(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.

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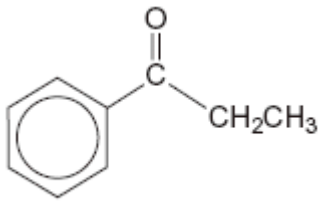
(2)
(Total 18 marks)

11 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.

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(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**.

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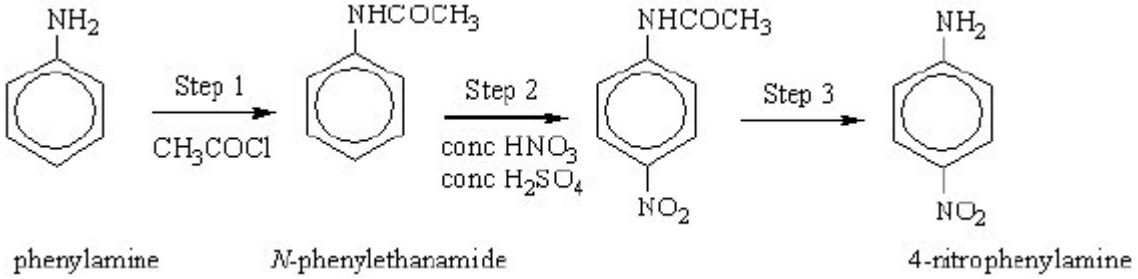
(2)
(Total 8 marks)

12 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.

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

(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.

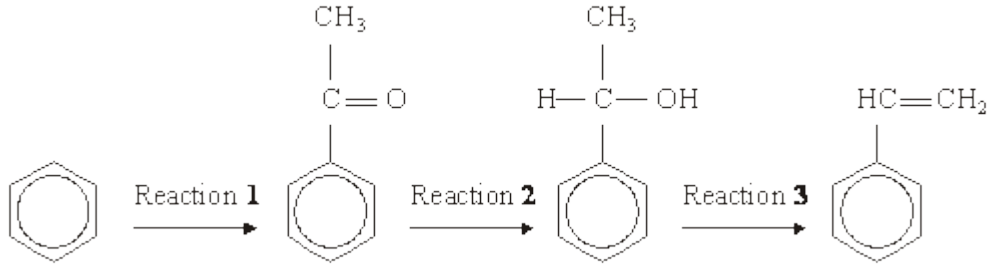
(5)

(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)

13 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**.

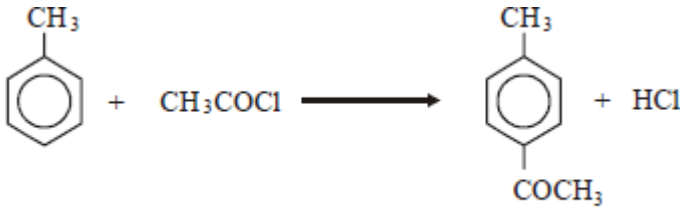
(6)

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

(2)

(Total 14 marks)

14 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)

15 (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)

16 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

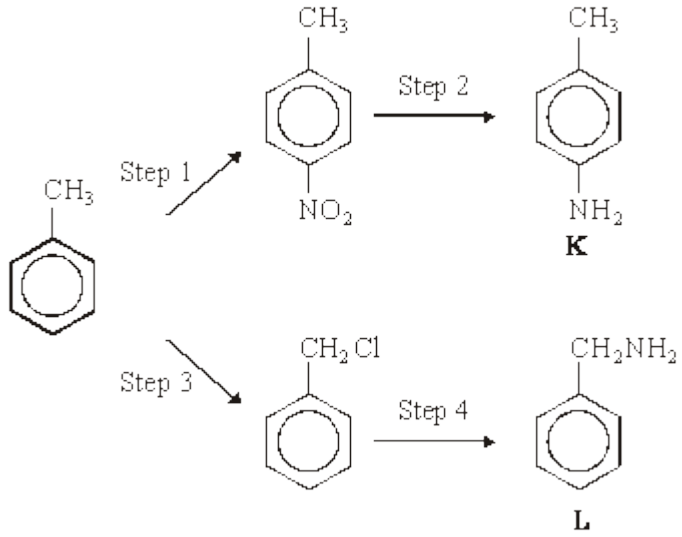
B 3.33 g

C 3.65 g

D 12.34 g

(Total 1 mark)

17 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 .....

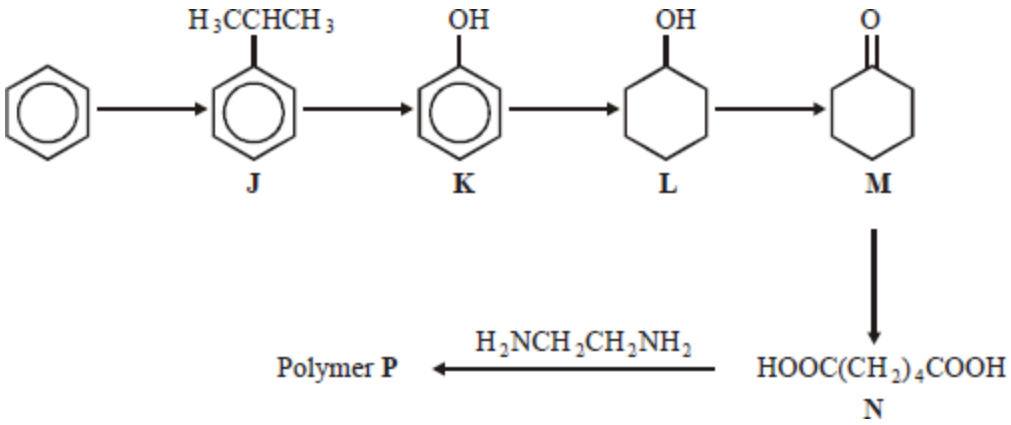
(ii) Name and outline a mechanism for Step 4.

Name of mechanism .....

Mechanism

(7)
(Total 15 marks)

18 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)

19 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)

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

A 164

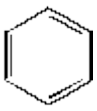
B 166

C 168

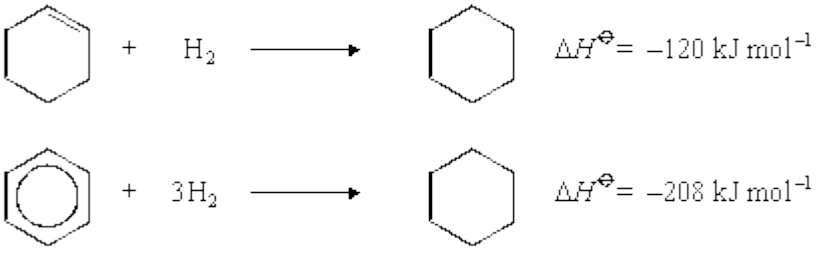
C 170

(Total 1 mark)

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

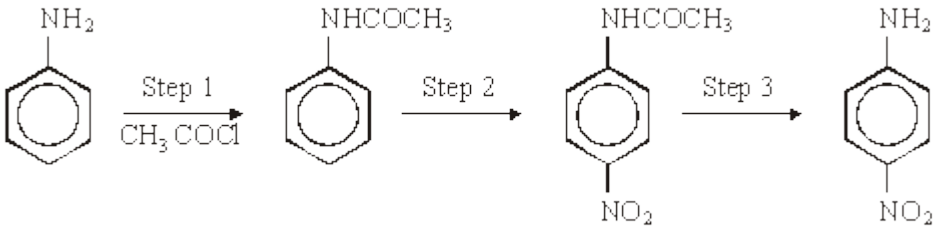


Give a reason for this difference in stability.



(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)

22 (a) Outline a mechanism for the reaction of $CH_3CH_2CH_2CHO$ with HCN and name the product.

Mechanism

Name of product .....

(5)

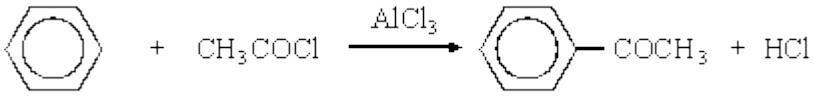
(b) Outline a mechanism for the reaction of CH_3OH with CH_3CH_2COCl and name the organic product.

Mechanism

Name of organic product .....

(5)

(c) An equation for the formation of phenylethanone is shown below. In this reaction a reactive intermediate is formed from ethanoyl chloride. This intermediate then reacts with benzene.



(i) Give the formula of the reactive intermediate.

.....

(ii) Outline a mechanism for the reaction of this intermediate with benzene to form phenylethanone.

(4)
(Total 14 marks)

23 (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)

24 (a) The reaction between aqueous persulphate ions, $S_2O_8^{2-}(aq)$, and iodide ions, $I^-(aq)$, is catalysed by $Fe^{2+}(aq)$ ions. Suggest why this reaction has a high activation energy.

Write equations to explain the catalytic action of $Fe^{2+}(aq)$ ions.

Suggest why $V^{3+}(aq)$ ions will also act as a catalyst for this reaction but $Mg^{2+}(aq)$ ions will not.

(6)

(b) Outline a mechanism for the reaction between benzene and ethanoyl chloride and explain why $AlCl_3$ acts as a Lewis acid catalyst for this reaction. Predict, with an explanation in each case, the suitability of $FeCl_3$ and of NH_4Cl to act as a catalyst for this reaction.

(9)

(Total 15 marks)

25 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

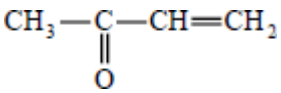
B 16.80 g

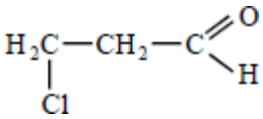
C 9.30 g

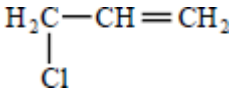
D 9.24 g

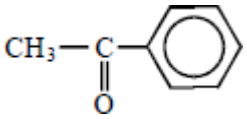
(Total 1 mark)

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

A 

B 

C 

D 

(Total 1 mark)

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

A poly(propene)

B benzene

C graphite

D sodium

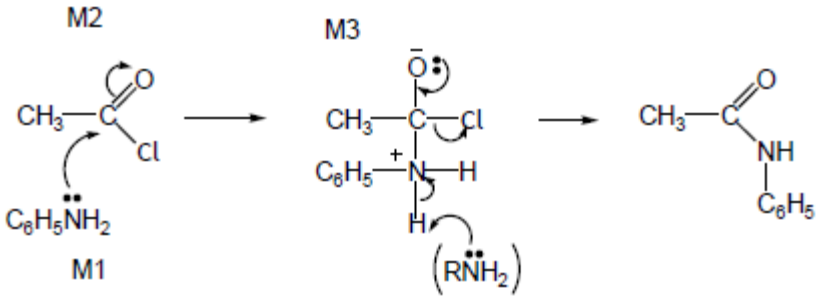
(Total 1 mark)

1

(a) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

1



Allow C_6H_5 or benzene ring

Allow attack by :$NH_2C_6H_5$

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

M3 for correct structure <u>with charges</u> but lone pair on O is part of M4

M4 (for three arrows and lone pair) can be shown in more than one structure

4

(b) **The minimum quantity of hot water was used:**

To ensure the hot solution would be saturated / crystals would form on cooling

1

The flask was left to cool before crystals were filtered off:

Yield lower if warm / solubility higher if warm

1

The crystals were compressed in the funnel:

Air passes through the sample not just round it

Allow better drying but not water squeezed out

1

A little cold water was poured through the crystals:

To wash away soluble impurities

1

(c) Water

Do not allow unreacted reagents

1

Press the sample of crystals between filter papers

Allow give the sample time to dry in air

1

(d) M_r product = 135.0

1

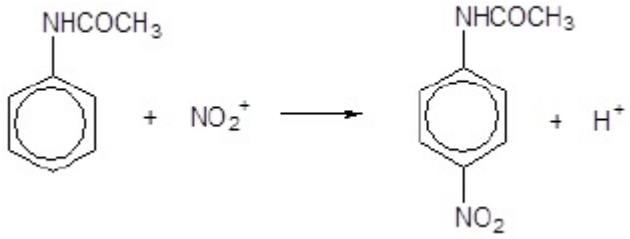
Expected mass = $5.05 \times \frac{135.0}{93.0} = 7.33$ g

1

Percentage yield = $\frac{4.82}{7.33} \times 100 = 65.75 = 65.8(\%)$

Answer must be given to this precision

(e)



OR

$C_6H_5NHCOCH_3 + NO_2^+ \rightarrow C_6H_4(NHCOCH_3)NO_2 + H^+$

1

(f) Electrophilic substitution

1

(g) Hydrolysis

1

(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

2

(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^+

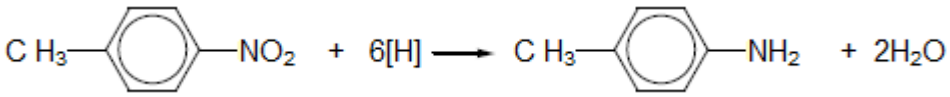
Ignore NaOH after Sn / HCl

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

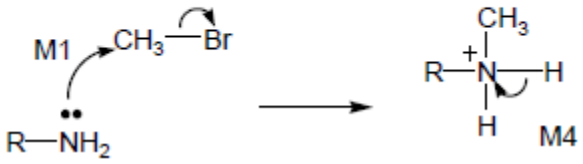
OR making fabric softener

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]

3

(a) (i) 3(-120) − (-208) = -152
OR
3(120) − 208 = 152 (kJ mol^{-1})

Must show working and answer and maths must be correct, but ignore sign

1

(ii) Electrons delocalised OR delocalisation (QOL)
OR
allow reference to resonance (QOL)

1

(b) x, y, w

Must be in this order

1

(c) (i) -240 (kJ mol^{-1})

Must have minus sign

1

(ii) between -239 and -121 (kJ mol^{-1})

Must have minus sign

1

(iii) Must specify which diene:

Proximity − for 1,3 C=C bonds are close together

allow converse for 1,4 diene

M1

1

Delocalisation − for 1,3 some delocalisation
OR
some overlap of electrons, π clouds or p orbitals

allow converse for 1,4 diene

M2

1

some extra stability for the 1,3- isomer

M3

1

[8]

4

(a) Hydrogen bond(ing)

Allow H bonding.

Penalise mention of any other type of bond.

1

(b) (i) Ammonia is a nucleophile

Allow ammonia has a lone pair.

1

Benzene repels nucleophiles

Allow (benzene) attracts / reacts with electrophiles.

***OR** benzene repels electron rich species or lone pairs.*

***OR** C–Cl bond is short / strong / weakly polar.*

1

(ii) H_2 / Ni **OR** H_2 / Pt **OR** Sn / HCl **OR** Fe / HCl

Ignore dil / conc of HCl.

Ignore the term 'catalyst'.

Allow H_2SO_4 with Sn and Fe but not conc.

Ignore NaOH following correct answer.

Not $NaBH_4$ nor $LiAlH_4$.

1

(iii) <u>conc HNO_3</u>

<u>conc H_2SO_4</u>

1

If either or both conc missed can score 1 for both acids.

1

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

OR using two equations

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

$H_2NO_3^+ \longrightarrow H_2O + NO_2^+$

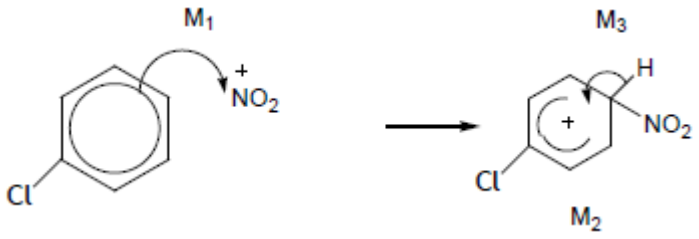
Allow 1:1 equation.

$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$.

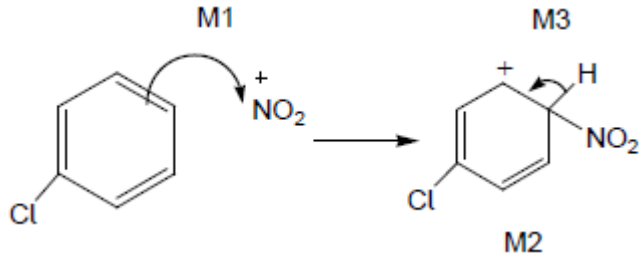
1

(iv) <u>Electrophilic substitution</u>

1



OR

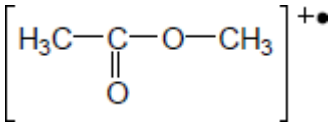


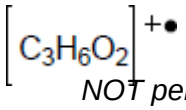
- *Ignore position or absence of Cl in M1 but must be in correct position for M2.*
- *M1 arrow from within hexagon to N or <u>+ on N</u>.*
- *Allow NO_2^+ in mechanism.*
- *Bond to NO_2 must be to N for structure mark M2.*
- *Gap in horseshoe must be centered around correct carbon (C1).*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6).*
- *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

[11]

5

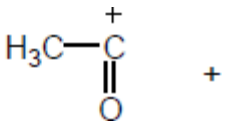
(a) 

OR 

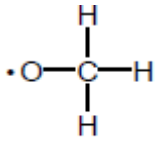
NOT penalise missing brackets.

If wrong ester, no further mark.

1

→  +

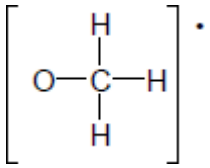
Must be displayed formula



(1)

Radical dot must be on O
Ignore lone pair(s) on O in addition to single electron

Allow radical with brackets as



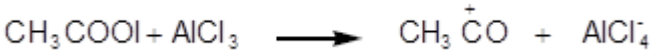
Ignore errors in acylium ion.

1

(b) (i) $AlCl_3$ or $FeCl_3$

If wrong no further marks.

1



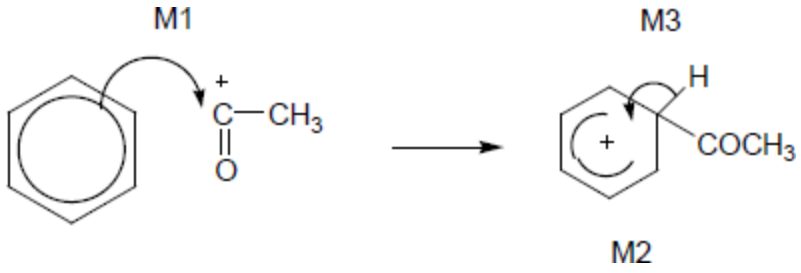
Correct equation scores 2 - contrast with (b)(iii)
Allow + on C or O in equation.

1

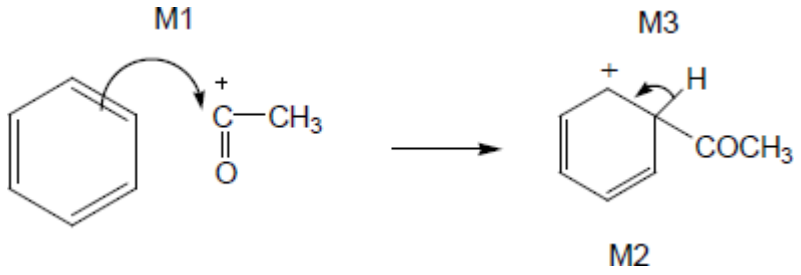
(ii) Electrophilic substitution

Ignore Friedel crafts.

1



OR

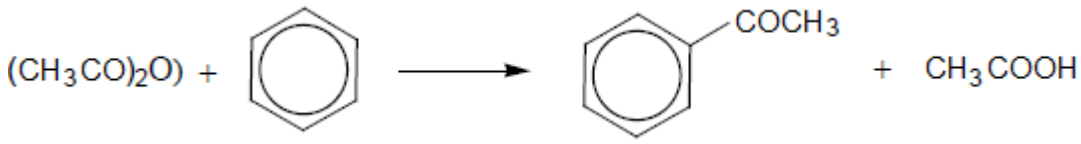


- *+ must be on C of RCO here*
- *M1 arrow from within hexagon to C or to + on C*
- *Gap in horseshoe must approximately be centred around C1 and not extend towards C1 beyond C2 and C6*
- *+ not too close to C1*
- *M3 arrow into hexagon unless Kekule*
- *allow M3 arrow independent of M2 structure, i.e. + on H in intermediate loses M2 not M3*
- *ignore base removing H for M3*

3

(iii) $(CH_3CO)_2O + C_6H_6 \longrightarrow C_6H_5COCH_3 + CH_3COOH$

OR



Correct equation scores 1 – contrast with (b)(i)

Not allow molecular formula for ethanoic anhydride or ethanoic acid.

1

[9]

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

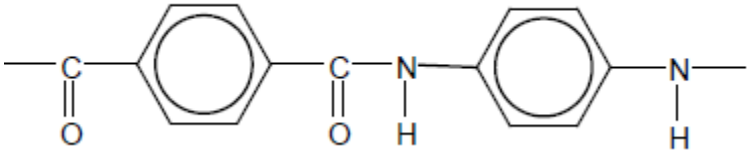
1

$\rightarrow C_6H_8N_2 + 4H_2O$

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°

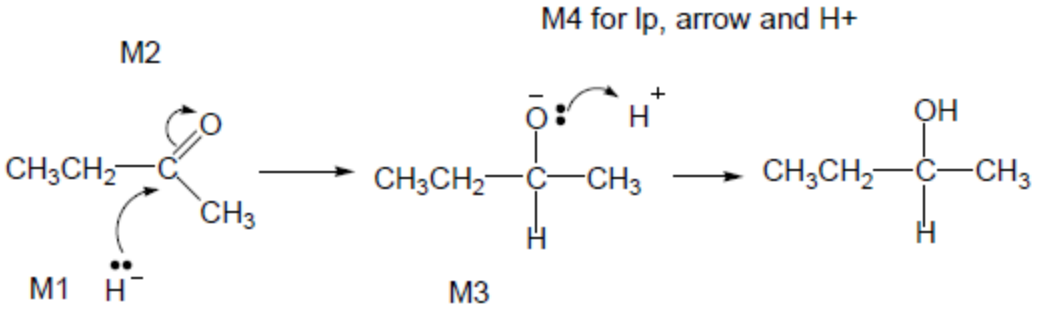
Allow 108° - 110°

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) $CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$

Allow RHS as $CH_3-\overset{\delta+}{C}(=O)\cdots Cl\cdots \overset{\delta-}{AlCl_3}$

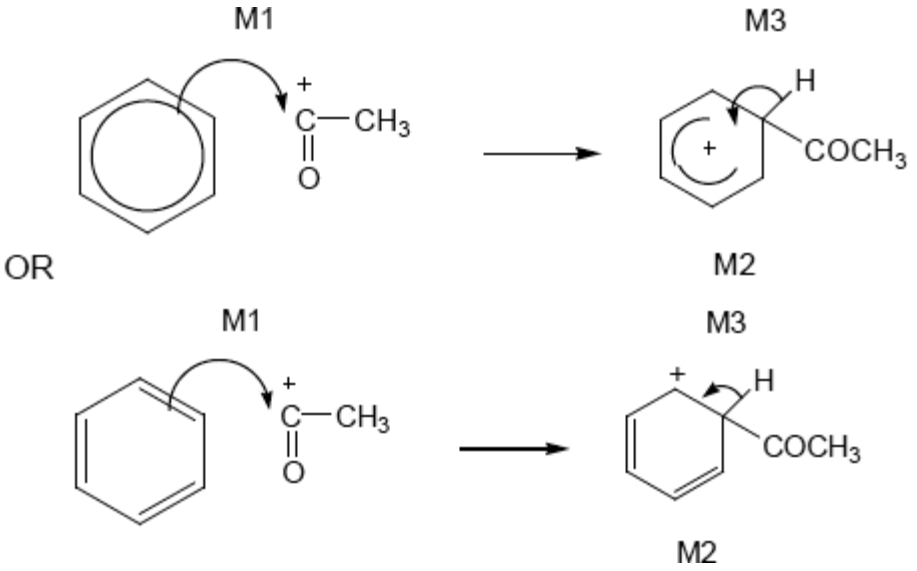
Allow + on C or O in equation but + must be on C in mechanism below

Ignore curly arrows in equation even if wrong.

1

$AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$

1



- *M1 arrow from within hexagon to C or to + on C*
- *+ must be on C of RCO in mechanism*
- *+ in intermediate not too close to C1*
- *gap in horseshoe must be centred approximately around C1*
- *M3 arrow into hexagon unless Kekule*
- *allow M3 arrow independent of M2 structure*
- *ignore base removing H for M3*
- ***NO** mark for name of mechanism*

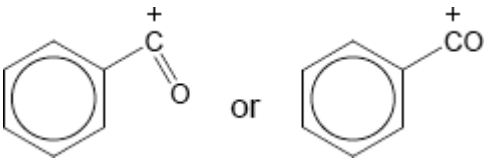
3

Phenylethanone ignore 1 in name, penalise other numbers

Note: this is the sixth marking point in (a)

1

(b)



+ must be on C

But allow $[C_6H_5CO]^+$

1

(c) M1 about electrons

methyl group has (positive) inductive effect OR increases electron density on benzene ring OR pushes electrons OR is electron releasing

Ignore reference to delocalisation

1

M2 about attraction

electrophile attracted more

or benzene ring better nucleophile

Allow intermediate ion stabilised

M2 only awarded after correct or close M1

1

[9]

8 (a) (i) 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

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

1

OR $H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + NO_2^+ + H_2O$

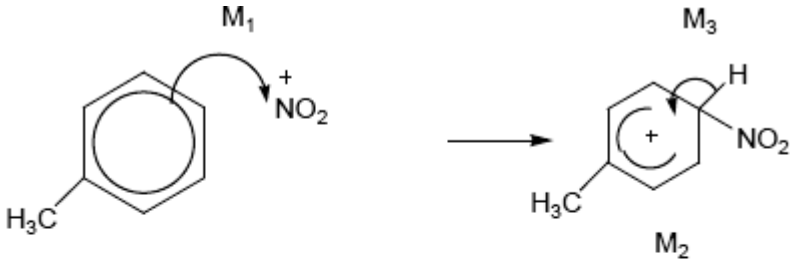
Allow + anywhere on NO_2^+

OR via two equations

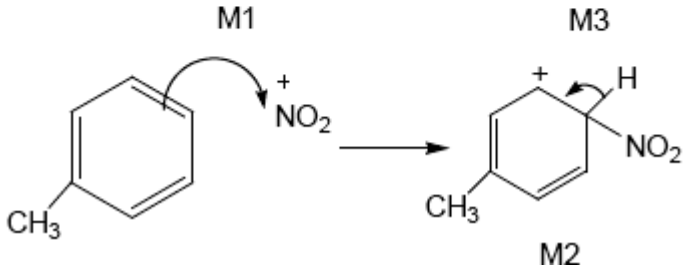
$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + H_2NO_3^+$

$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$

(ii)



OR



- *ignore position or absence of methyl group in M1 but must be in correct position for M2*
- *M1 arrow from within hexagon to N or <u>+ on N</u>*
- *Allow NO_2^+ in mechanism*
- *Bond to NO_2 must be to 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*
- *+ on H in intermediate loses M2 not M3*

3

(b) 5

1

(c) 2

1

(d) $2C_7H_5N_3O_6 \longrightarrow 5H_2O + 3N_2 + 7C + 7CO$

Or halved

1

[9]

9

(a) **M1** Benzene is <u>more stable than cyclohexatriene</u>

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

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

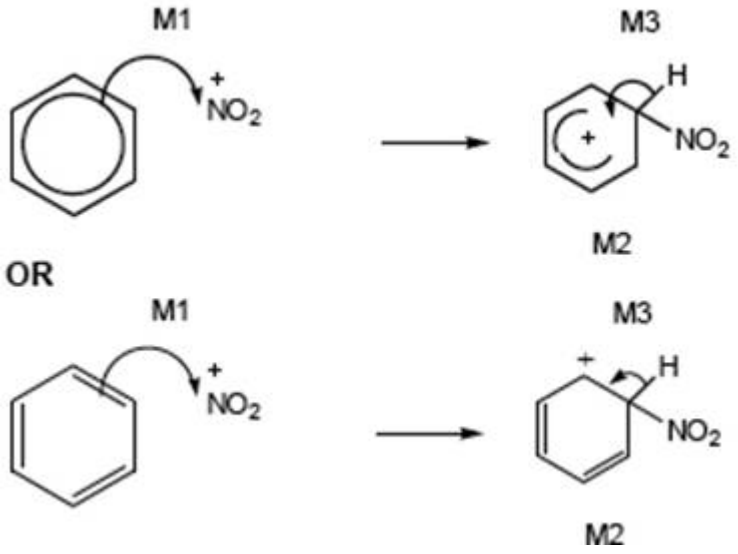
OR via two equations

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

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



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

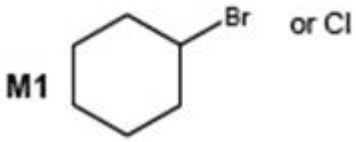
allow M3 arrow independent of M2 structure

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)**

M1 

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]

10 (a) (i) $C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$

OR

$C_6H_6 + CH_3CH_2CO^+ \rightarrow C_6H_5COCH_2CH_3 + H^+$

allow C_2H_5

penalise $C_6H_5–CH_3CH_2CO$

allow + on C or O in equation

1

Phenylpropanone

OR ethylphenylketone **OR** phenylethylketone

Ignore 1 in formula, but penalise other numbers

1

$AlCl_3$

can score in equation

1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$

allow C_2H_5

allow + on C or O in equation

1

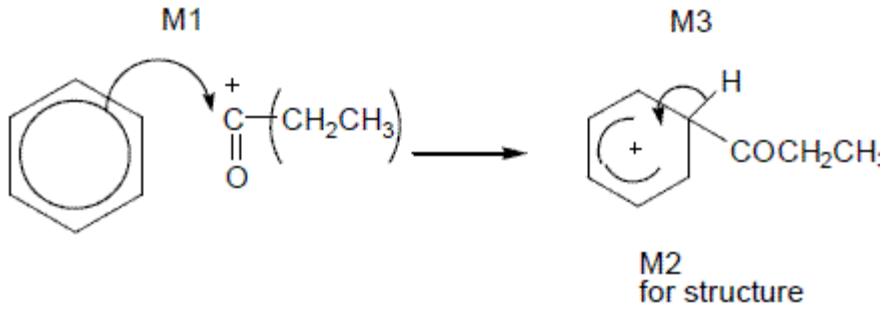
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

1

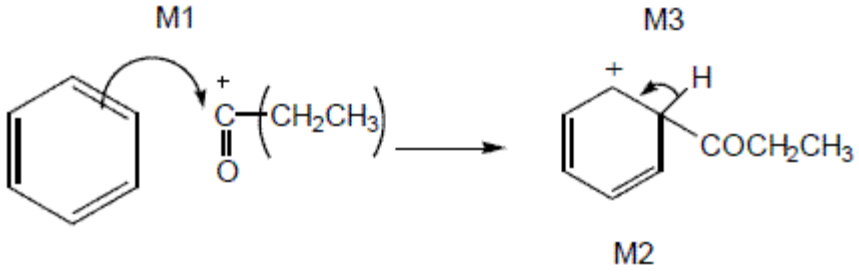
(ii) electrophilic substitution

can allow in (a)(i) if no contradiction

1



OR



M1 arrow from circle or within it to C or to + on C
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1

M2 penalise C_6H_5–CH_3CH_2CO (even if already penalized in (a)(i))

M3 arrow into hexagon unless Kekule

allow M3 arrow independent of M2 structure

ignore base removing H in M3

3

(b) (i) $CH_3CH_2\underline{CHO} + HCN \rightarrow CH_3CH_2CH(OH)CN$ **OR** $C_2H_5CH(OH)CN$

aldehyde must be –CHO brackets optional

1

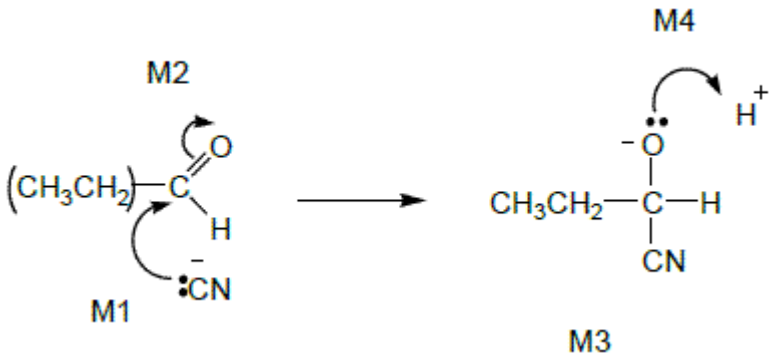
2-hydroxybutanenitrile **OR** 2-hydroxybutan<u>o</u>nitrile

no others

1

(ii) nucleophilic addition

1



M1 includes lp and arrow to Carbonyl C and minus charge (on either C or N)

Not allow M2 before M1, but allow M1 to C^+ after non-scoring carbonyl arrow

Ignore δ+, δ– on carbonyl group, but if wrong way round or full + charge on C lose M2

M3 for correct structure including minus sign. Allow C_2H_5

M4 for lp and curly arrow to H^+

4

(iii) (propanone) slower ***OR*** <u>propanal</u> faster

1

inductive effects of alkyl groups
OR
C of C=O less δ+ in propanone
OR
alkyl groups in ketone hinder attack
OR
easier to attack at end of chain

if wrong, no further marks

1

[18]

11 (a) CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride
OR $(CH_3CH_2CO)_2O$ OR propanoic anhydride
penalize contradiction in formula and name e.g. propyl chloride

could score in equation

1

$AlCl_3$ or $FeCl_3$ or names

could score in equation

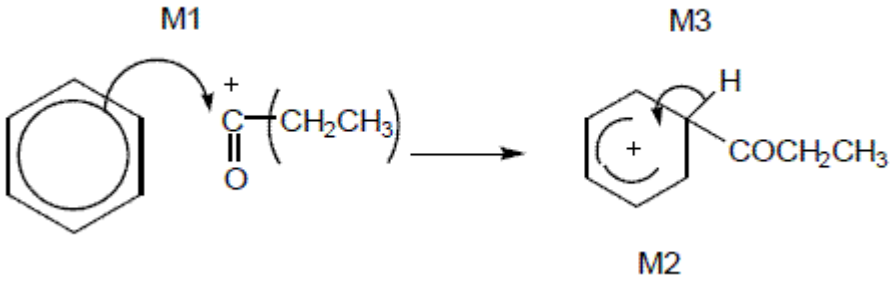
1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$
Allow RCOCl in equation but penalise above

allow + on C or O in equation

1

(b)



M1 arrow from circle or within it to C or to + on C

Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1

M3 arrow into hexagon unless Kekule

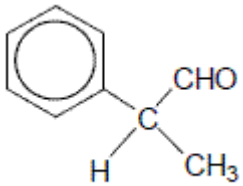
allow M3 arrow independent of M2 structure

Ignore base removing H in M3

3

(c) Tollens or ammoniacal silver nitrate

1



penalise wrong formula

1

[8]

12

Mark Range	The marking scheme for this part of the question includes an overall assessment for the Quality of Written Communication (QWC). There are no discrete marks for the assessment of QWC but the candidates' QWC in this answer will be one of the criteria used to assign a level and award the marks for this part of the question **Descriptor** an answer will be expected to meet most of the criteria in the level descriptor
4-5	– claims supported by an appropriate range of evidence – good use of information or ideas about chemistry, going beyond those given in the question – argument well structured with minimal repetition or irrelevant points – accurate and clear expression of ideas with only minor errors of grammar, punctuation and spelling
2-3	– claims partially supported by evidence – good use of information or ideas about chemistry given in the question but limited beyond this – the argument shows some attempt at structure – the ideas are expressed with reasonable clarity but with a few errors of grammar, punctuation and spelling
0-1	– valid points but not clearly linked to an argument structure – limited use of information or ideas about chemistry – unstructured – errors in spelling, punctuation and grammar or lack of fluency

(a) (i) M_r of $C_6H_5NH_2$ = 93 M_r of CH_3COCl = 78.5
total M_r of reagents = 264.5

1

$$\% \text{ atom economy} = \frac{M_r \text{ of wanted product}}{\text{total } M_r \text{ of all reagents}} \times 100 \text{ QWC}$$

1

$$= \frac{135}{264.5} \times 100 = 51.0\ \%$$

1

(ii) expected yield = $\frac{10}{93}$ × 0.5 × 135 = 7.26 kg

1

% yield = $\frac{5.38}{7.26}$ × 100 = 74.1 %

1

(iii) Although yield appears satisfactory (74%) % atom economy is only 51% QWC

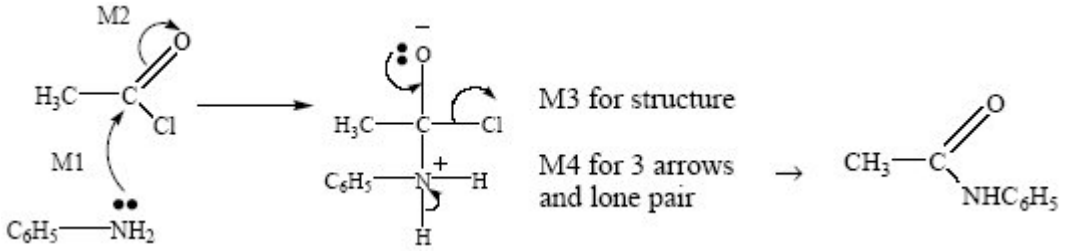
1

nearly half of the material produced is waste and must be disposed of QWC

1

(b) (nucleophilic) addition-elimination

1

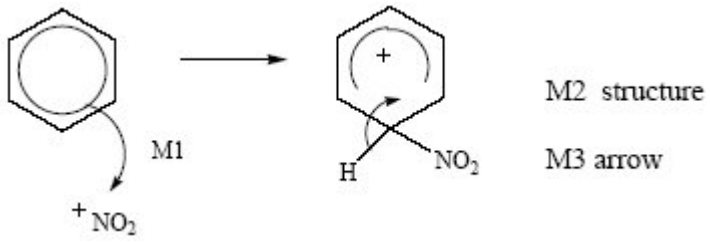


QWC (2)

4

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

1



3

[16]

13

(a) $CH_3COCl + AlCl_3 \rightarrow CH_3\overset{+}{C}O + AlCl_4^-$

(1) equation (1)

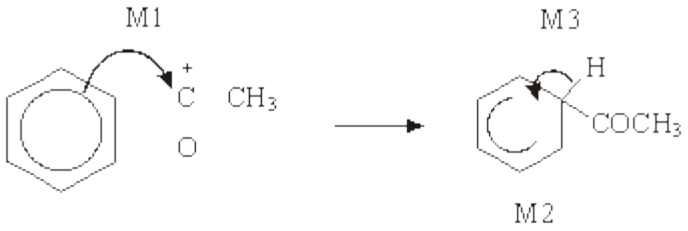
2

penalise wrong alkyl group once at first error
position of + on electrophile can be on O or C or outside [ ]
penalise wrong curly arrow in the equation or lone pair on $AlCl_3$ else ignore

Electrophilic substitution

NOT F/C acylation

1



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

M1 arrow from within hexagon to C or to + on C

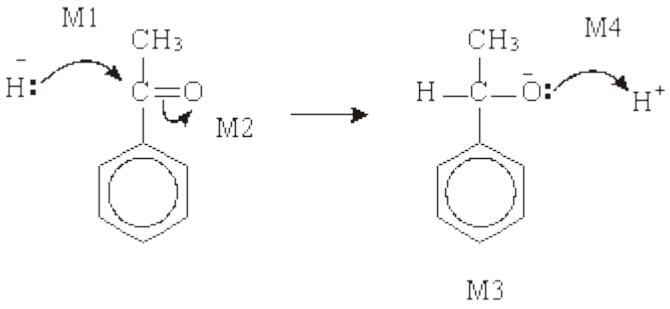
+ must be on C of $\overset{+}{\text{RCO}}$

3

(b) Nucleophilic addition

NOT reduction

1



M2 not allowed independent, but can allow M1 for attack of H^- on C+ formed

4

1–phenylethan(–1–)ol or (1–hydroxyethyl)benzene

1

(c) dehydration or elimination

1

(conc) H_2SO_4 or (conc) H_3PO_4

allow dilute and Al_2O_3

Do not allow iron oxides

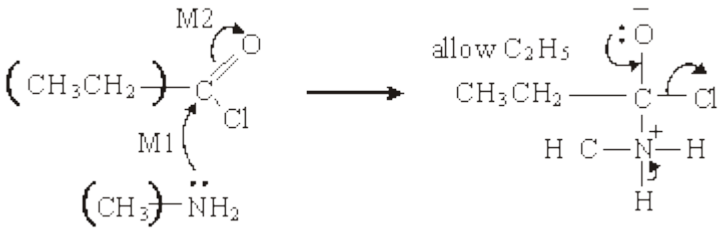
1

[14]

14 C

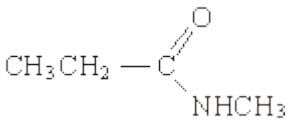
[1]

15 (a) (nucleophilic) addition-elimination;



(M3 for structure)
(M4 for 3 arrows and lone pair)
(M2 not allowed independent of M1, but allow M1 for correct attack on C+ if M2 show as independent first.)
(+on C of C=O loses M2 but ignore δ+ if correct)
(Cl^- removing Ft loses M4)

1



(If MS lost above for wrong C chain, do not penalise same error again here)

5

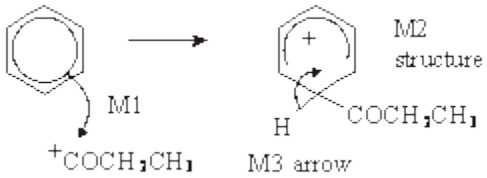
(b) $CH_3CH_2COCl + AlCl_3 \rightarrow [CH_3CH_2CO]^+ + AlCl_4^-$;

(penalise wrong alkyl group once at first error)

(position of + on electrophile can be on O or C or outside [ ])

(penalise wrong curly arrow in the equation or lone pair on $AlCl_3$)

1

	*(horseshoe must not extend beyond C2 to C6 but can be smaller)* *(+ not too close to C1)* *(penalise M2 if CH_3 chain wrong again but allow M1 and M3)* *(M3 arrow into hexagon unless Kekule)*
(M1 arrow from within hexagon to C or to + on C) *(don't penalise position of + on C of RCO+)*	*(allow M3 arrow independent of M2 structure)*

3

$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$;

(or can be gained in mechanism);

1

(c) M1 $CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$ 1

(penalise wrong alkyl group once at first error)

1

M2 M_r of CH_3CH_2COCl = 92.5 1

(if Mr wrong, penalise M2 only)

1

M3 moles of CH_3CH_2COCl = 1.48/92.5 = 0.016 1

1

M4 moles NaOH = 2 × 0.016 = 0.032 1

(allow for × 2 conseq to wrong no of moles)

1

M5 volume of NaOH = 0.032/0.42 = 0.0762 dm^3 or 76.2 cm^3 1

(with correct units)

(if ×2 missed in M4 lose M5 also)

1

[16]

16 B

[1]

17 (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

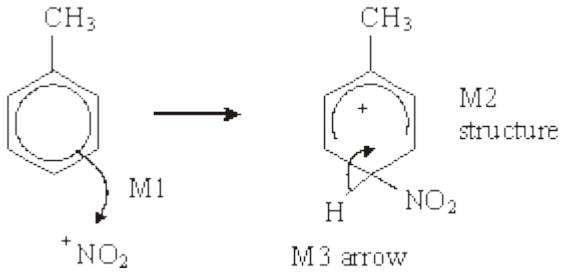
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

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

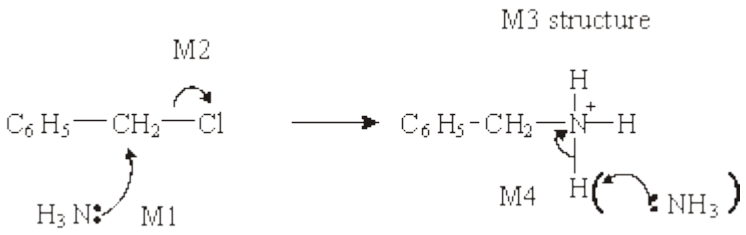
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

1



4

[15]

18 A **[1]**

19 D **[1]**

20 B **[1]**

21 (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

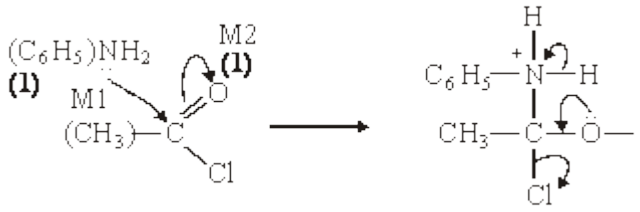
(b) (i) phenylamine weaker **(1)**

if wrong no marks

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

3

(ii) addition – elimination **(1)**



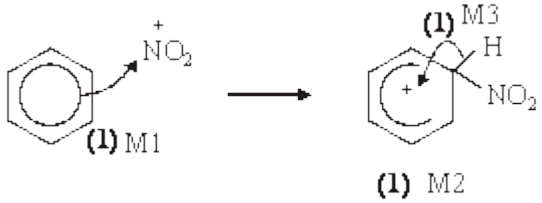
*structure **(1)** M3*
*3 arrows **(1)** M4*

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

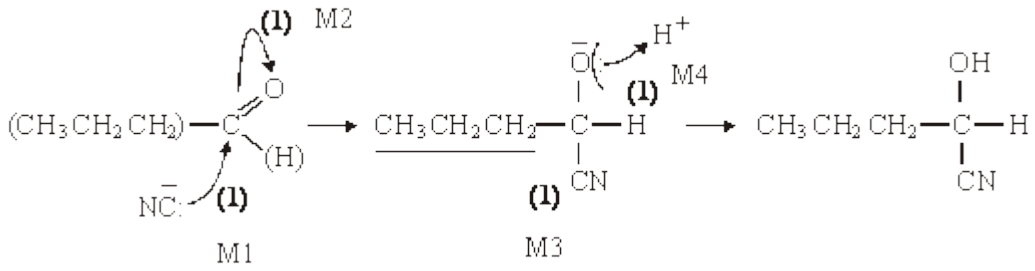
(iii) **No marks for name of mechanism in this part**
if conc missing can score one for both acids (or in equation)
allow two equations

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]

22 (a) *Mechanism*



Allow C_3H_7 if structure shown elsewhere

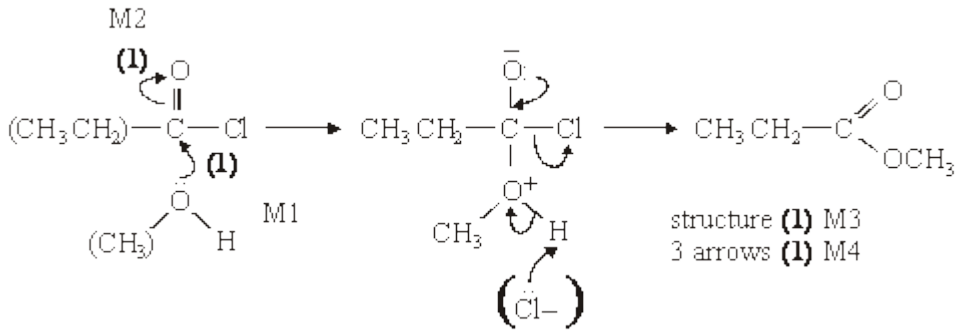
penalise HCN splitting if wrong

Name of product: 2-hydroxypenta(neo)nitrile **(1)**

or 1-cyanobutan-1-ol

5

(b) *Mechanism*

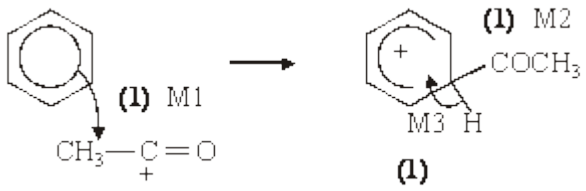


Name of organic product: methylpropanoate **(1)**

5

(c) (i) ([] CH_3CO [])$^+$ **(1)**

(ii)



4

Notes

(abc) extra curly arrows are penalised

(a) be lenient on position of negative sign on : CN^- but arrow must come from lp

(a)/(b)  alone loses M2 but can score M1 for attack on C+, similarly 

(a) allow 2-hydroxypentanonitrile or 2-hydroxypenta(ne)nitrile ... pentylnitrile

(b) in M4, allow extra: Cl^- attack on H, showing loss of H^+

(c) (i) allow formula in an "equation"(balanced or not)
be lenient on the position of the + on the formula

(ii) for M1 the arrow must go to the C or the + on the C
don't be too harsh about the horseshoe, but + must not be close to the saturated C
M3 must be final step not earlier; allow M3 even if structure (M2) is wrong

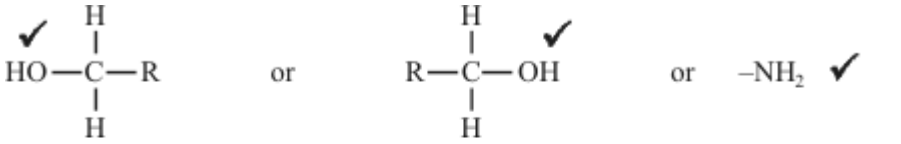
[14]

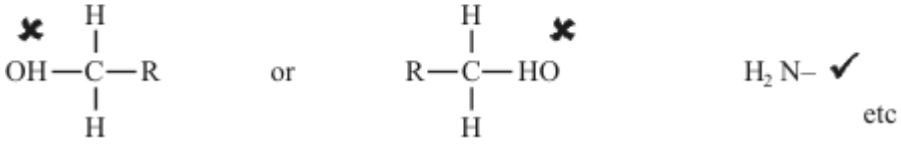
Organic points

(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

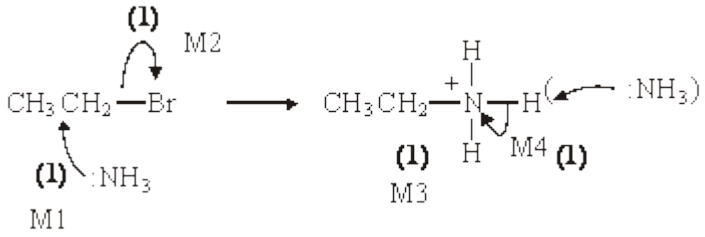




Penalise once per paper

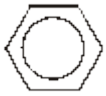
allow CH_3– or –CH_3 or  or CH_3
or H_3C–

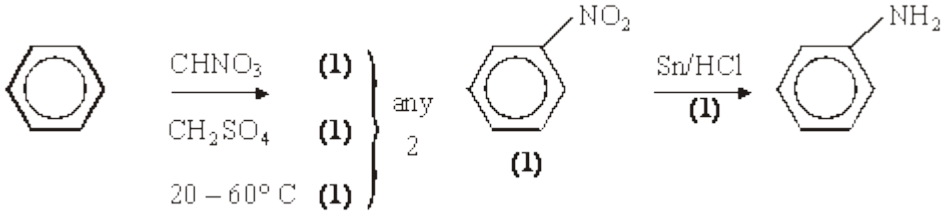
23 (a)



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

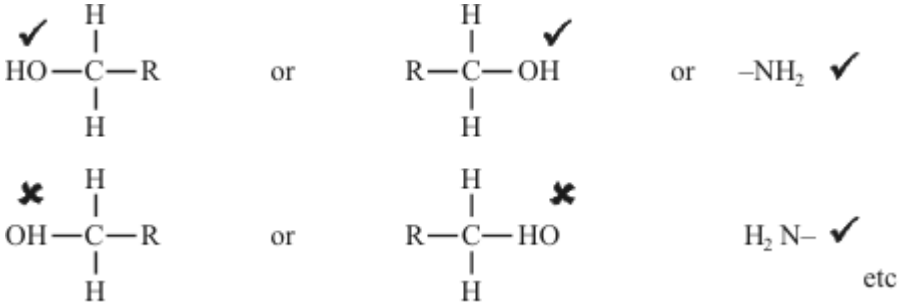
[11]

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–

24 (a) High E_a: $S_2O_8^{2-}$ repels I^- **or** both ions negative **(1)**

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ **(1)**

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ **(1)**

N.B. Ignore additional incorrect equations

Vanadium is a transition element **or** Magnesium is not a transition element **(1)**

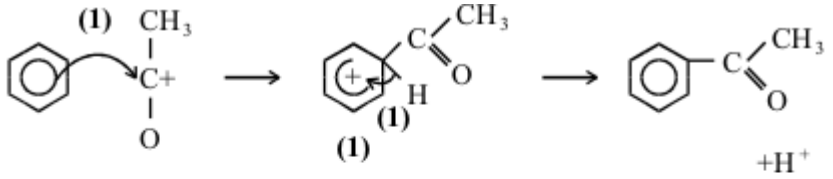
Vanadium has variable oxidation states **(1)**

Magnesium only forms Mg^{2+}, **or** has only one oxidation state **(1)**

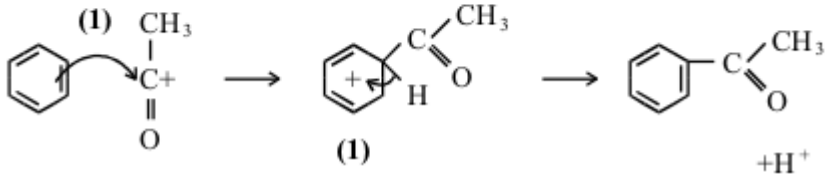
N.B. Score two marks for "Only vanadium has variable oxidation states"

6

(b) $AlCl_3 + Cl\text{-}COCH_3 \rightarrow AlCl_4^- + CH_3CO^+$ **(1)**



or



$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ **(1)**

Lewis acid: $AlCl_3$ accepts electron pair

N.B. penalise incorrect acyl chloride by one
N.B. penalise chloroethane by two marks i.e. first equation mark, attack on benzene mark

NH_4Cl: Not a catalyst **(1)**

$FeCl_3$: A catalyst **(1)**
has a low energy vacant shell
or has spaces or vacancies in d shell
or has a partially filled d shell
or able to accept an electron pair
or can form $FeCl_4^-$ **(1)**

9

[15]

25 D **[1]**

26 B **[1]**

27 A **[1]**