AQA A2 CHEMISTRY

TOPIC 4.6

AROMATIC CHEMISTRY

TOPIC 4.7

AMINES

BOOKLET OF PAST EXAMINATION QUESTIONS

1. (a) Benzene reacts with nitric acid in the presence of a catalyst to form nitrobenzene. This is an electrophilic substitution reaction.

(i) Write an equation for the overall reaction.

.....

(1)

(ii) State the name of the catalyst used.

.....

(1)

(iii) Write the formula, including its charge, of the electrophile involved in the reaction.

.....

(1)

(b) Methylbenzene is converted into (chloromethyl)benzene in a free radical substitution reaction.

$$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$$

(i) Write an equation for the initiation step.

.....

(1)

(ii) Write equations for the **two** propagation steps.

(2)

(iii) Give the formula of another possible organic product of the reaction.

.....

(1)

(c) The equations below both represent addition reactions.

Reaction 1 $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

Reaction 2 $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

(i) Write a mechanism for **Reaction 1**.

(3)

(ii) State **one** important difference between the mechanism for **Reaction 2** and that for **Reaction 1.**

.....

.....

(2)

(d) Crude oil is a complex mixture of compounds. Most of these are hydrocarbons although there are also sulphur compounds present. Some of the hydrocarbon fractions of crude oil are catalytically cracked.

(i) What is the economic importance of cracking?

.....

.....

(1)

(ii) The alkane, $C_{14}H_{30}$, can be cracked to give an alkene and an alkane. Write a balanced equation to show one way in which this could happen.

.....

(1)

(iii) Why is it important that as many as possible of the sulphur compounds are removed from fuels obtained from oil?

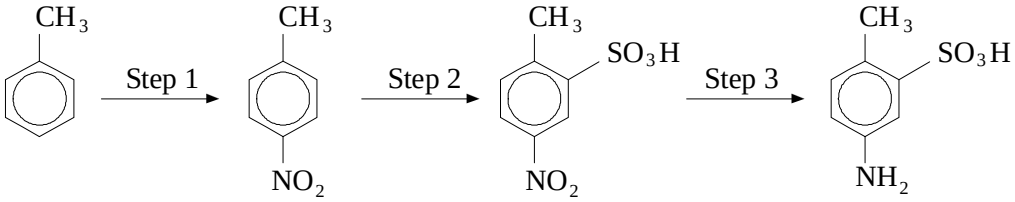
.....

.....

(1)

(Total 15 marks)

2. 5-Amino-2-methylbenzenesulphonic acid can be obtained from methylbenzene in a three-step synthesis:



(a) For each step below, name the type of reaction taking place and suggest a suitable reagent or combination of reagents.

Step 1

Type of reaction .....

Reagent(s) .....

Step 3

Type of reaction .....

Reagent(s) .....

(4)

(b) Write an equation for the formation of the reactive inorganic species involved in the mechanism in Step 1.

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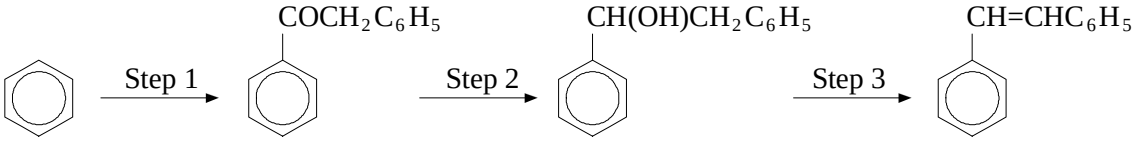
(2)

(Total 6 marks)

3. Consider the following reaction sequence:



(a) Give the reagents required to carry out Step 1 and write an equation for the formation of the reactive intermediate involved. Name and outline the mechanism for the reaction between this intermediate and benzene.

Reagents .....

.....

Equation for formation of reactive intermediate .....

.....

Name of mechanism .....

Mechanism

(8)

(b) Name the type of reaction taking place in Step 2 and suggest a suitable reagent or combination of reagents.

Type of reaction .....

Reagent(s) .....

(2)

(c) Suggest a suitable reagent for Step 3 and name the mechanism for this reaction.

Reagents .....

Name of mechanism .....

(2)

(d) What type of stereoisomerism is shown by the product of Step 2?

.....

(1)

(e) Name the type of isomerism shown by the final product, 1,2-diphenylethene, and explain why this compound can exist in two stereoisomeric forms.

Type of isomerism .....

Explanation .....

.....

(2)

(Total 15 marks)

4. Compound **X**, $(CH_3)_2CHCN$, can be formed from a haloalkane, C_3H_7Br.

(a) (i) Name compound **X**.

.....

(ii) Give the reagent and conditions necessary to form **X** from C_3H_7Br.

Reagent.....

Conditions.....

(iii) Name and outline the mechanism for this reaction, showing clearly the structure of C_3H_7Br.

Name of mechanism.....

Mechanism

(7)

(b) Give the reagents required to form nitrobenzene from benzene. Name the mechanism involved and write an overall equation for the reaction.

Reagents.....

Name of mechanism.....

Equation

(4)

(c) By referring to the structures of the organic compounds, explain why the inorganic reagent used in part (a)(ii) will react with C_3H_7Br but will not react with benzene.

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.....

(3)
(Total 14 marks)

5. (a) (i) Give the name of the type of mechanism involved in the reaction between propanal and hydrogen cyanide.

.....

(1)

(ii) Give the name and graphical formula of the product formed by the reaction given in (a)(i).

Name .....

Graphical formula

(2)

(b) (i) Write an equation for the reaction between 1-bromopropane and potassium cyanide.

.....

(1)

(ii) Give the name of the type of mechanism involved in the reaction in (b)(i).

.....

(1)

(c) The mechanisms of the reactions in (a)and (b) involve the same inorganic attacking species. Give the formula of this species and state what feature of its structure is responsible for its role.

Formula .....

Structural feature .....

(2)

(d) Give the reagent and conditions and state the type of mechanism involved in each of the following conversions.

Benzene into methylbenzene.

Reagent .....

Conditions .....

Type of mechanism .....

(4)
(Total 11 marks)

6. (1-Methylpropyl)benzene, $C_6H_5CH(CH_3)CH_2CH_3$, is the major organic product obtained when benzene and but-l-ene react together in the presence of aluminium chloride and hydrogen chloride.

(a) Write an equation showing the formation of the major carbonium ion obtained from but-l-ene, aluminium chloride and hydrogen chloride.

.....

.....

(2)

(b) Name the mechanism involved in the reaction between benzene and the carbonium ion formed in part (a) above.

.....

(1)

(c) Explain why butylbenzene, $C_6H_5CH_2CH_2CH_2CH_3$, is obtained only as a minor by-product in the above reaction between benzene and but-l-ene.

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(3)

(d) Explain why only one organic product is obtained when but-2-ene is used instead of but-l-ene in the reaction with benzene.

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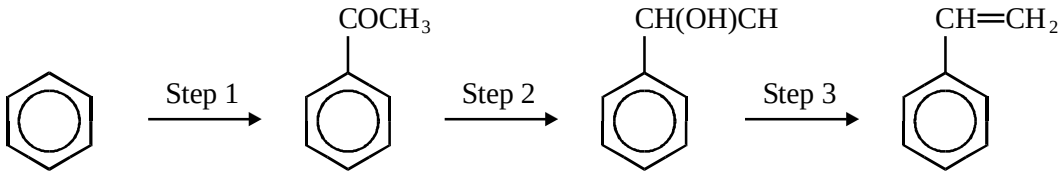
(1)

(e) Give the structure of a compound, other than an alkene, which could be used to make (1-methylpropyl)benzene from benzene in the presence of aluminium chloride.

(1)
(Total 8 marks)

7. (a) In the laboratory, phenylethene can be obtained from benzene in a three-step synthesis:



(i) Give the organic reagent and the inorganic catalyst used in Step 1.

Reagent .....

Catalyst .....

(ii) Name the type of reaction taking place in Step 2.

.....

(iii) Suggest either a reagent or a combination of reagent and catalyst suitable for the conversion in Step 2.

.....

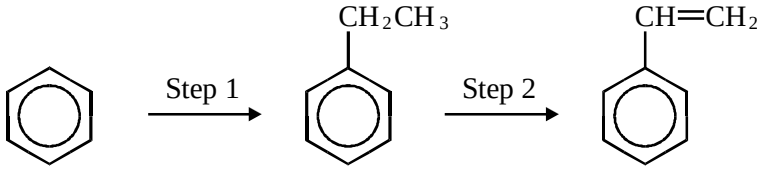
(iv) For Step 3, name the type of reaction and suggest a suitable reagent for the reaction.

Type of reaction .....

Reagent .....

(6)

(b) In industry, phenylethene is made from benzene and ethene in a two-step process:



(i) Give one major use of phenylethene.

.....

(ii) Identify the reactive species which attacks benzene in Step 1 and write an equation to show how this species is generated.

Reactive species .....

Equation .....

(iii) Name the type of reaction which occurs in Step 2.

.....

(4)
(Total 10 marks)

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

Mechanism

Name of product .....

(5)

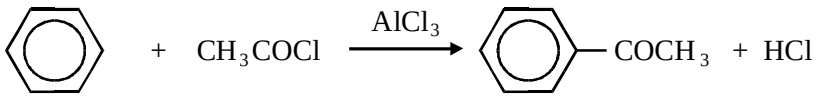
(b) Outline a mechanism for the reaction of CH_3OH with CH_3CH_2COCl and name the organic product.

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.

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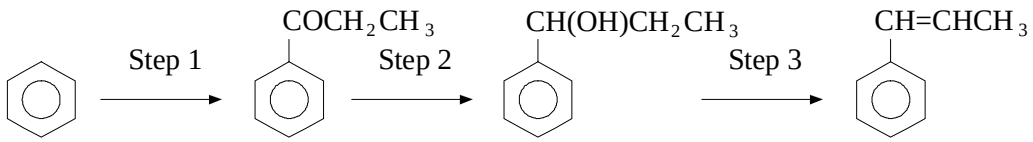
(ii) Outline a mechanism for the reaction of this intermediate with benzene to form phenylethanone.

(4)
(Total 14 marks)

9. Consider the following reaction sequence:



(a) For each step, name the type of reaction taking place and suggest a suitable reagent or combination of reagents.

Step 1

Type of reaction.....

Reagent(s).....

Step 2

Type of reaction.....

Reagent(s).....

Step 3

Type of reaction.....

Reagent(s).....

(7)

(b) What type of stereoisomerism is shown by the product of Step 2?

.....

(1)

(c) Explain why the final product, 1-phenylpropene, is formed as a mixture of two isomers.

.....

.....

.....

(2)

(d) When 1-phenylpropene is treated with hydrogen bromide, two compounds are formed which are structural isomers.

(i) Give the structures of the two isomers.

Isomer 1 *Isomer 2*

(ii) Name the type of mechanism involved.

.....

(iii) By reference to the structures of the two carbonium ion intermediates formed, suggest why the two isomers are obtained in unequal amounts.

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.....

(6)
(Total 16 marks)

10. (a) Name the compound $(CH_3)_2NH$

.....

(1)

(b) $(CH_3)_2NH$ can be formed by the reaction of an excess of CH_3NH_2 with CH_3Br. Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(5)

(c) Name the type of compound produced when a large excess of CH_3Br reacts with CH_3NH_2 Give a use for this type of compound.

Type of compound .....

Use .....

(2)

(d) Draw the structures of the two compounds formed in the reaction of CH_3NH_2 with ethanoic anhydride.

(2)
(Total 10 marks)

11. (a) Name and outline a mechanism for the formation of butylamine, $CH_3CH_2CH_2CH_2NH_2$, by the reaction of ammonia with 1-bromobutane, $CH_3CH_2CH_2CH_2Br$.

Name of mechanism .....

Mechanism

(5)

(b) Butylamine can also be prepared in a two-step synthesis starting from 1-bromopropane, $CH_3CH_2CH_2Br$. Write an equation for each of the two steps in this synthesis.

Step 1

.....

Step 2

.....

(3)

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

.....

.....

.....

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

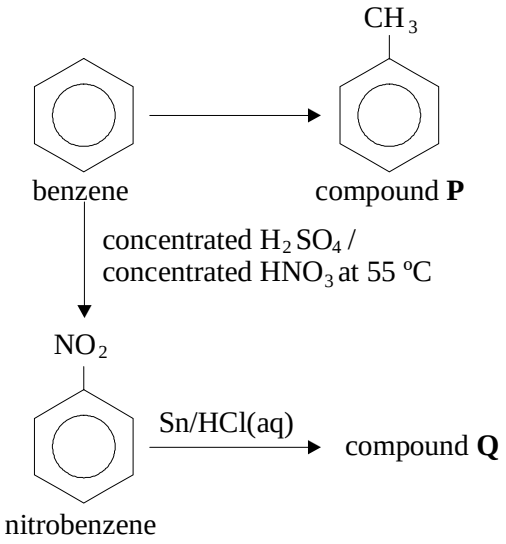
.....

(3)

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

(1)
(Total 12 marks)

12. The figure shows a reaction scheme for some aromatic compounds.



(a) (i) Give the reagents and conditions for the conversion of benzene into compound **P**.

.....

.....

(3)

(ii) Give the name of the mechanism of this reaction.

.....

(2)

(b) Draw the graphical formulae of the possible organic products when excess chlorine is passed through boiling compound **P** in strong sunlight.

(3)

(c) (i) Classify the type of reaction occurring when nitrobenzene is converted into compound **Q**.

.....

(1)

(ii) Draw the graphical formula of compound **Q**.

(2)

(d) Classify the types of reaction and draw the graphical formulae of the organic products of the reaction of propanal with:

(i) sodium tetrahydridoborate(III), $NaBH_4$;

Type of reaction .....

(2)

(ii) Fehling's solution;

Type of reaction .....

(2)

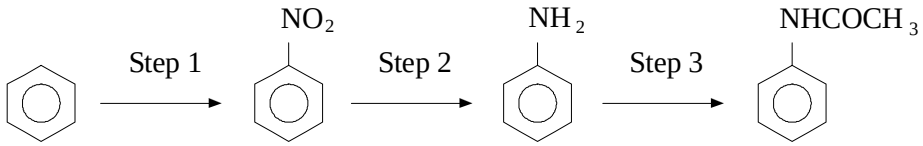
(iii) hydrogen cyanide.

Type of reaction .....

(2)

(Total 17 marks)

13. *N*-Phenylethanamide can be prepared from benzene in three steps:



(a) Give the reagents required to carry out Step 1 and write an equation for the formation of the reactive inorganic species present. Name and outline the mechanism for the reaction between this species and benzene.

Reagents.....

Equation for formation of reactive species.....

.....

Name of mechanism.....

Mechanism

(7)

(b) Name the type of reaction taking place in Step 2 and suggest a suitable reagent or combination of reagents.

Type of reaction.....

Reagent(s).....

(2)

(c) Write an equation for the reaction occurring in Step 3. Name and outline the mechanism for this reaction.

Equation

Name of mechanism.....

Mechanism

(7)
(Total 16 marks)

14. (a) Explain how methylamine can act as a Brønsted-Lowry base.

.....

.....

(2)

(b) Explain why phenylamine is a weaker base than ammonia.

.....

.....

(2)

(c) (i) Name the type of mechanism involved when methylamine is formed from bromomethane and ammonia.

.....

(ii) Give the structures of three organic compounds other than methylamine which can be obtained from the reaction between an excess of bromomethane and ammonia.

Compound 1 *Compound 2* *Compound 3*

(iii) Name the type of compound formed in part (c)(ii) which can be used as a cationic surfactant.

.....

(5)
(Total 9 marks)

15. (a) (i) Write an equation for the formation of ethylamine from ethanenitrile.

.....

(ii) Suggest a suitable reagent or a combination of reagent and catalyst for this reaction.

.....

(2)

(b) State the type of reaction taking place between ethylamine and an excess of bromoethane. Give the structures of the three organic products obtained from this reaction.

Type of reaction.....

Product 1 *Product 2* *Product 3*

(4)

(c) Suggest a mechanism to show how molecules of ethylamine and hydrogen bromide react together.

(3)

(d) Explain why phenylamine is a weaker base than ethylamine.

.....

.....

.....

(2)

(e) Suggest why ethanamide, CH_3CONH_2, is a weaker base than ethylamine.

.....

.....

.....

(2)

(f) Write an equation for the formation of the compound $CH_3CONHCH_2CH_3$ from ethylamine and a suitable reagent. Name and outline the mechanism for this reaction.

Equation .....

Name of mechanism .....

Mechanism

(7)
(Total 20 marks)

16. (a) Methylamine is a weak Brønsted-Lowry base and can be used in aqueous solution with one other substance to prepare a basic buffer.

(i) Explain the term *Brønsted-Lowry base* and write an equation for the reaction of methylamine with water to produce an alkaline solution.

Brønsted-Lowry base .....

Equation .....

(ii) Suggest a substance that could be added to aqueous methylamine to produce a basic buffer.

.....

(iii) Explain how the buffer solution in part (a)(ii) is able to resist a change in pH when a small amount of sodium hydroxide is added.

.....

.....

.....

(5)

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

.....

.....

.....

(2)

(c) A cation is formed when methylamine reacts with a large excess of bromoethane. Name the mechanism involved in the reaction and draw the structure of the cation formed.

Name of mechanism .....

Structure

(2)
(Total 9 marks)

17. (Phenylmethyl)amine, $C_6H_5CH_2NH_2$, can be prepared from (bromomethyl)benzene, $C_6H_5CH_2Br$, and also from benzenecarbonitrile, C_6H_5CN.

(a) (i) Write an equation for the conversion of (bromomethyl)benzene into (phenylnethyl)amine. Name the type of reaction taking place and explain why a low yield of product is obtained.

Equation

Type of reaction .....

Explanation .....

.....

.....

(ii) Name the type of reaction involved in the conversion of benzenecarbonitrile into (phenylmethyl)amine. Write an equation for this reaction and suggest a suitable reagent or a combination of reagent and catalyst. Explain why this method of preparation gives a high yield of product.

Type of reaction. .....

Equation

Reagent(s) .....

Explanation .....

.....

.....

(9)

(b) State which of the two amines, (phenylmethyl)amine and phenylamine, $C_6H_5NH_2$, is the weaker base, and explain your choice.

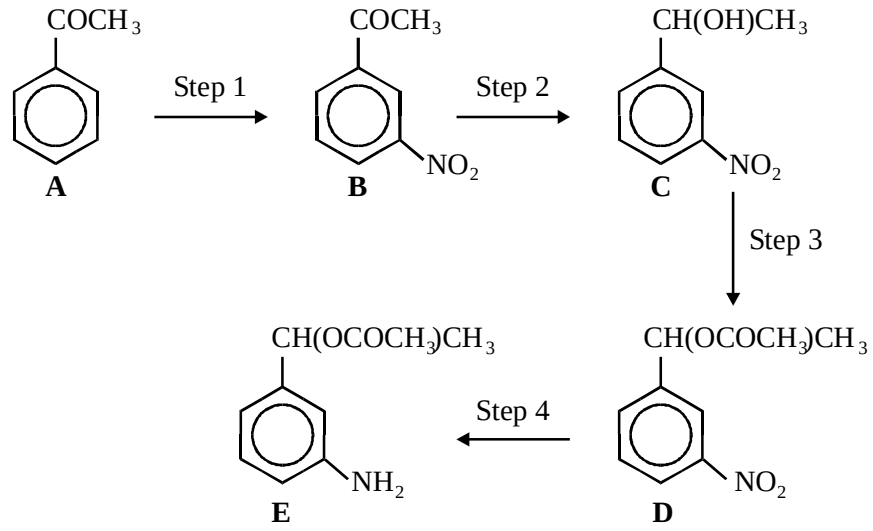
Weaker base .....

Explanation .....

(3)

(Total 12 marks)

18. Consider the following reaction sequence:



(a) (i) Give the reagents required to carry out Step 1 and write an equation for the formation of the inorganic reactive intermediate involved.

Reagents.....

Equation for formation of inorganic reactive intermediate.....

.....

(ii) Name and outline the mechanism for the reaction between this intermediate and compound **A.**

Name of mechanism.....

Mechanism

(7)

(b) Name the type of reaction taking place in Step 2 and suggest a suitable reagent or combination of reagents for this conversion.

Type of reaction.....

Reagent(s).....

(2)

(c) Suggest a derivative of ethanoic acid which could be used as a reagent for carrying out Step 3. Name and outline the mechanism for this reaction. You may use ROH to represent compound **C** in the mechanism.

Reagent.....

Name of mechanism.....

Mechanism

(6)

(d) Name the type of reaction taking place in Step 4 and suggest a suitable reagent or combination of reagents for this conversion.

Reagent.....

Name of mechanism.....

(2)

(e) What type of stereoisomerism is shown by compound **E**?

.....

(1)

(Total 18 marks)

19. (a) (i) What feature of the ammonia molecule allows it to act as a base?

.....

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

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(iii) Explain why phenylamine is a weaker base than ammonia.

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.....

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(5)

(b) (i) Write an equation for the hydrogenation of propanenitrile to form propylamine. Give an example of a suitable catalyst for this reaction.

Equation.....

Catalyst.....

(ii) Name the mechanism involved when propylamine is made from 1-bromopropane and ammonia.

.....

(iii) Explain why the propylamine obtained in part (b)(ii) is not the only organic product formed.

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.....

(5)

(c) Give the structure of the nitrogen-containing compound formed in the reaction between propylamine and ethanoic anhydride.

(1)

(d) The secondary amine $CH_3(CH_2)_{11}NHCH_3$ can be converted into a cationic surfactant by reaction with an excess of chloromethane. Name the type of product formed and give the structural formula of the compound.

Type of product.....

Structural formula

(3)
(Total 14 marks)

20. (a) Explain why phenylamine. $C_6H_5NH_2$. is a weaker base than cyclohexylamine, $C_6H_{11}NH_2$.

.....

.....

.....

.....

.....

(3)

(b) Write an equation for the formation of cyclohexylamine from bromocyclohexane and an excess of ammonia. Name and outline the mechanism of this reaction.

Equation

Name of mechanism .....

Mechanism

(6)

(c) (i) Give the reagent used to convert bromocyclohexane into cyanocyclohexane, $C_6H_{11}CN$.

.....

(ii) Suggest a suitable reagent or combination of reagents for converting cyanocyclohexane into $C_6H_{11}CH_2NH_2$. Name the type of reaction involved and write an equation for the conversion.

Reagent(s) .....

Type of reaction .....

Equation .....

.....

(4)

(d) Write an equation for the reaction between an excess of cyclohexylamine and ethanoyl chloride. Name and outline the mechanism for this reaction.
You may use RNH_2 to represent cyclohexylamine.

Equation .....

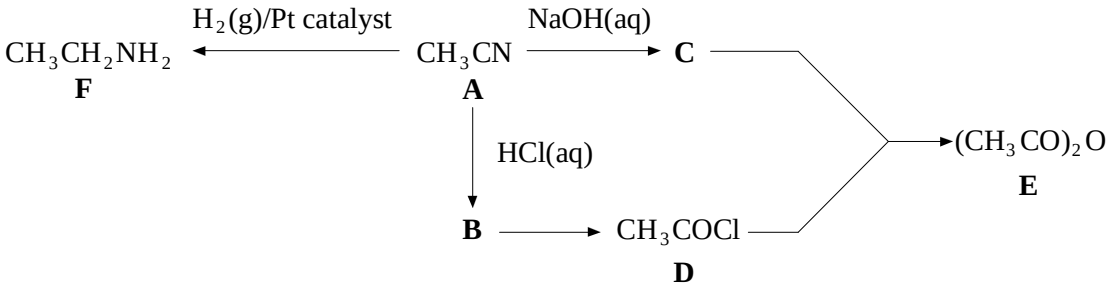
.....

Name of mechanism .....

Mechanism

(7)
(Total 20 marks)

21. Consider the following reaction scheme and answer the questions below.



(a) The reaction of compound **C** with **D** produces compound **E**.

(i) Draw the graphical structure of **E**.

(1)

(ii) State the compound type to which **E** belongs.

.....

(1)

(b) Compound **F** may be prepared by the reaction of **A** with hydrogen gas in the presence of a platinum catalyst.

(i) Give the name of **F**.

.....

(1)

(ii) Suggest the type of reaction involved in the conversion of **A** into **F**.

.....

(1)

(c) Compounds **D** and **F** react readily together. Write an equation for the reaction between them.

.....

(2)

(Total 6 marks)

22. (a) Explain why ethylamine is a stronger base than ammonia.

.....

.....

.....

(3)

(b) Give a suitable reagent or combination of reagents for the formation of ethylamine from ethanenitrile. Name the type of reaction involved and write an equation for the conversion.

Reagent(s) .....

Type of reaction .....

Equation .....

(3)

(c) Give the structure of the final substitution product obtained when ethylamine reacts with an excess of bromoethane. Name the type of compound formed and suggest a use for this type of product.

Structure

Name .....

Use .....

(3)

(d) Name and outline a mechanism for the reaction between ethylamine and ethanoyl chloride.

Name of mechanism .....

Mechanism

(5)

(e) Write an equation for the reaction between ethylamine and ethanoic anhydride.

.....

.....

.....

(1)

(Total 15 marks)

23. (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)

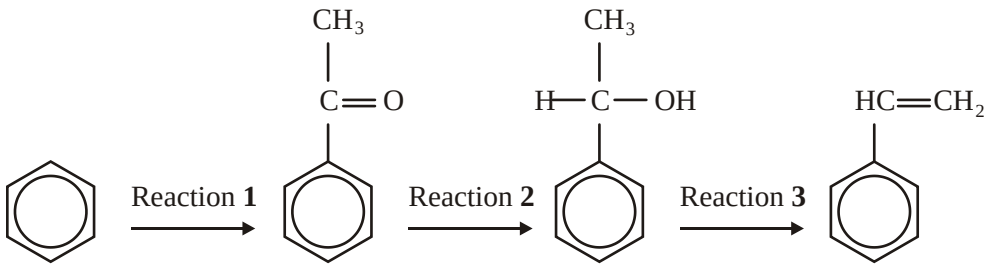
(b) Benzene reacts with propanoyl chloride in the presence of aluminium chloride. Write equations to show the role of aluminium chloride as a catalyst in this reaction. Outline a mechanism for this reaction of benzene.

(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)

24. 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)

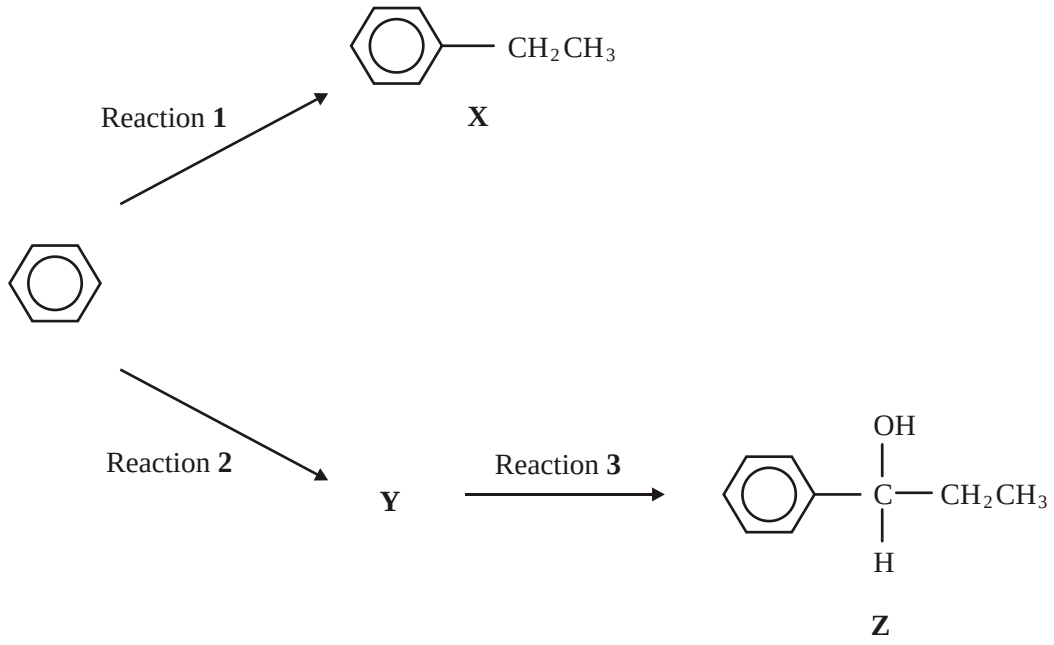
(b) $NaBH_4$ is a possible reagent for Reaction **2**.
Name and outline the mechanism for the reaction with $NaBH_4$ in Reaction **2**.
Name the product of Reaction **2**.

(6)

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

(2)
(Total 14 marks)

25. Two reactions of benzene are shown below.



(a) Name **X** and give the reagent and catalyst required for Reaction **1**.
Write an equation for the formation of the reactive intermediate involved in this reaction.
Name and outline a mechanism for the reaction of this reactive intermediate with benzene to form **X**.

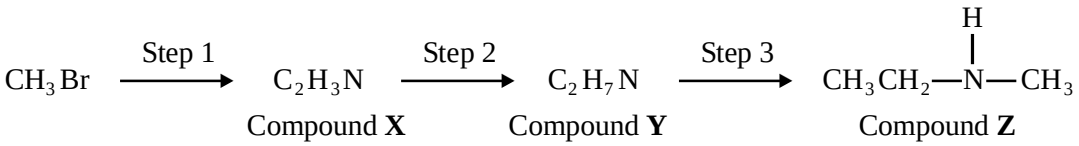
(8)

(b) (i) Deduce the structure of **Y** and give the organic reagent needed for Reaction **2**.

(ii) Give the reagent(s) needed for Reaction **3**.

(3)
(Total 11 marks)

26. Compound **Z** can be formed via compounds **X** and **Y** in the three step synthesis shown below.



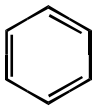
Identify compounds **X** and **Y** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **Z** is an example.

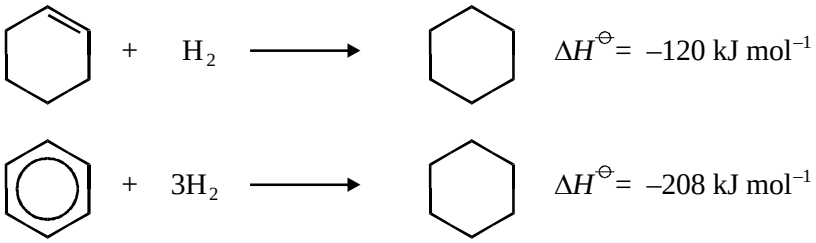
Compound **Z** reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

(Total 9 marks)

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

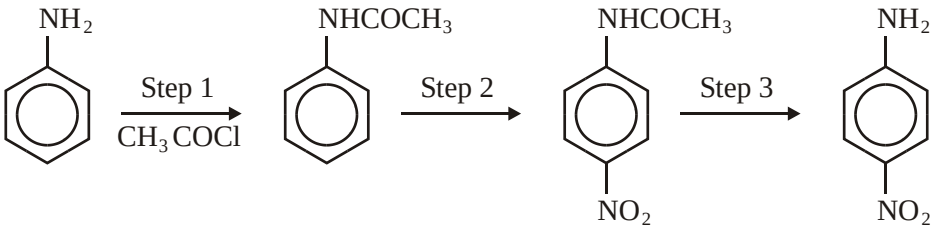


Give a reason for this difference in stability.



(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)