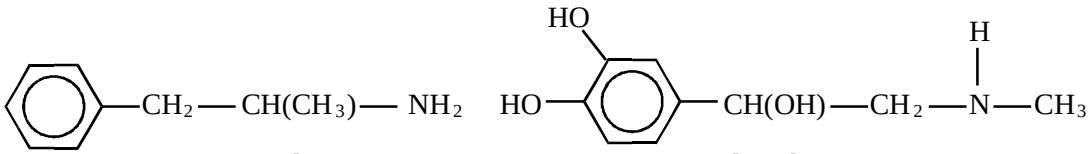
1. Adrenalin is a hormone which raises blood pressure, increases the depth of breathing and delays fatigue in muscles, thus allowing people to show great strength under stress.

Benzedrine is a pharmaceutical which stimulates the central nervous system in a similar manner to adrenalin.



Benzedrine

Adrenalin

(a) (i) On the structure for benzedrine mark with a (∗) any asymmetric carbon atom that causes chirality.

(1)

(ii) Suggest why adrenalin is more soluble in water than is benzedrine.

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(2)

(b) Give the structural formulae of the organic products obtained when benzedrine reacts with:

(i) an aqueous acid such as dilute hydrochloric acid;

(1)

(ii) ethanoyl chloride in the absence of a catalyst;

(1)

(iii) excess ethanoyl chloride in the presence of the catalyst anhydrous aluminium chloride.

(2)

(d) It is possible to eliminate a molecule of water from adrenalin which for the purpose of this question may be represented as R–CH(OH)–CH_2–NH–CH_3. Draw the structural formulae of the two stereoisomers produced.

(2)

(e) The mass spectra of both benzedrine and adrenalin have a peak at a mass/charge ratio of 44. Draw the structure of the species which give these peaks.

(i) in benzedrine;

(1)

(ii) in adrenalin.

(1)
(Total 11 marks)

2. (a) Define:

(i) the standard enthalpy of formation of benzene, $C_6H_6(l)$;

.....

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(2)

(ii) the standard enthalpy of combustion of benzene, $C_6H_6(l)$.

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(2)

(b) Calculate the standard enthalpy of formation of benzene, $C_6H_6(l)$, using the following enthalpy of combustion data:

Substance	$\Delta H_c^{\ominus}$/kJ mol^{-1}
$C_6H_6(l)$	–3273
$H_2(g)$	–286
C(s)	–394

(3)

(c) If the standard enthalpy of formation is calculated from average bond enthalpy data assuming that benzene has three C==C and three C—C bonds, its value is found to be +215 kJ mol^{-1}.
Explain, with reference to the structure and stability of benzene, why this value differs from that calculated in (b). Use an enthalpy level diagram to illustrate your answer.

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(4)

(d) Benzene reacts with bromine when gently warmed in the presence of a catalyst of anhydrous iron(III) bromide.

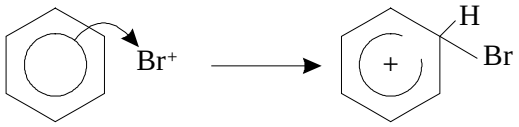
(i) The reaction is first order with respect to benzene and first order with respect to bromine. Write the rate equation for the reaction.

.....

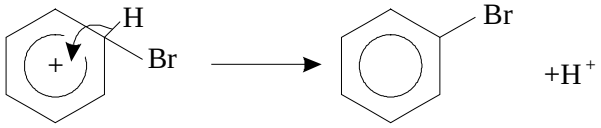
(1)

(ii) The mechanism of this reaction involves an attack by Br^+ followed by loss of H^+.

Step 1.



Step 2.



Deuterium, symbol D, is an isotope of hydrogen, and the C—D bond is slightly **stronger** than the C—H bond. If step 2 were the rate-determining (slower) step, suggest how the rate of this reaction would alter if deuterated benzene, C_6D_6, were used instead of ordinary benzene, C_6H_6, and explain your answer.

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(2)
(Total 14 marks)

3. Benzene, C_6H_6, reacts with ethanoyl chloride, CH_3COCl, by an electrophilic substitution reaction in the presence of aluminium chloride as a catalyst.

(a) Identify the electrophile involved in this reaction and write an equation to show its formation.

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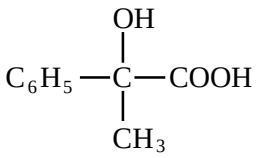
(2)

(b) Draw the mechanism for the electrophilic substitution of benzene by ethanoyl chloride.

(3)

(c) Suggest a reaction scheme, stating reagents and conditions, to convert the product of the above reaction into



(5)
(Total 10 marks)

4. (a) Pure copper is needed for electrical applications. The purity of a sample of copper can be found by reacting it with concentrated nitric acid, neutralising the resulting solution and treating it with excess potassium iodide. Iodine is liberated and this can be titrated with standard sodium thiosulphate solution. The reactions are:

$$Cu(s) + 4HNO_3(l) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(1)$$

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

A copper foil electrode from an electric cell weighs 1.74 g. It was made into 250 cm^3 of a solution of copper(II) ions. To 25.0 cm^3 of this solution excess iodide ions were added, and the mixture titrated with 0.100 mol dm^{-3} sodium thiosulphate solution. On average 26.8 cm^3 was required. Calculate the percentage purity of the copper foil.

(6)

(b) Copper(II) chloride is used as a catalyst in the reaction of benzenediazonium chloride in the presence of hydrochloric acid to give chlorobenzene:

$$C_6H_5N_2^+ Cl^- \rightarrow C_6H_5Cl + N_2$$

The catalytic effect of transition metals or their ions is often attributed to their having several stable oxidation states. Explain why such states are possible in transition metals and why they are important in catalysis.

(4)

(c) (i) State the reagents and conditions needed to make benzenediazonium chloride from phenylamine.

(2)

(ii) Explain why the temperature needs to be carefully controlled in the reaction in part (i).

(2)

(iii) Write the equation for the reaction of benzenediazonium chloride with phenol using structural formulae. Give the conditions under which benzenediazonium chloride reacts with phenol and state what you would see.

(5)

(d) Phenylamine is prepared from benzene. Give the reagents and conditions needed for each of the steps in the conversion of benzene to phenylamine.

(6)

(Total 25 marks)

5. (a) Benzene, C_6H_6, reacts with ethanoyl chloride, CH_3COCl, to give a compound of molecular formula C_8H_8O.

(i) Identify another substance that must be present for this reaction to occur and state the function of this substance in this reaction.

……...……..……..……..

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(2)

(ii) Give the mechanism for this reaction.

(4)

(b) Phenol, C_6H_5OH, reacts differently from benzene with ethanoyl chloride. State the type of reaction that would occur between phenol and ethanoyl chloride and give the structure of the organic product.

Type of reaction ..……

Structure of the organic product

(2)

(c) A benzene ring containing two hydroxy groups, $C_6H_4(OH)_2$, can exist as a range of isomers.

(i) Draw the structure of each isomer.

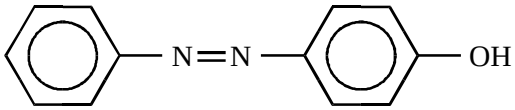
(2)

(ii) A polymer can be formed by reacting one of these isomers with the di-acyl chloride, $ClCOCH_2COCl$.

Draw a diagram indicating clearly the structure of such a polymer.

(2)

(d) The compound 4-hydroxyazobenzene



can be obtained from phenylamine and phenol in two steps. Identify the intermediate formed and give the reagents and conditions for each step.

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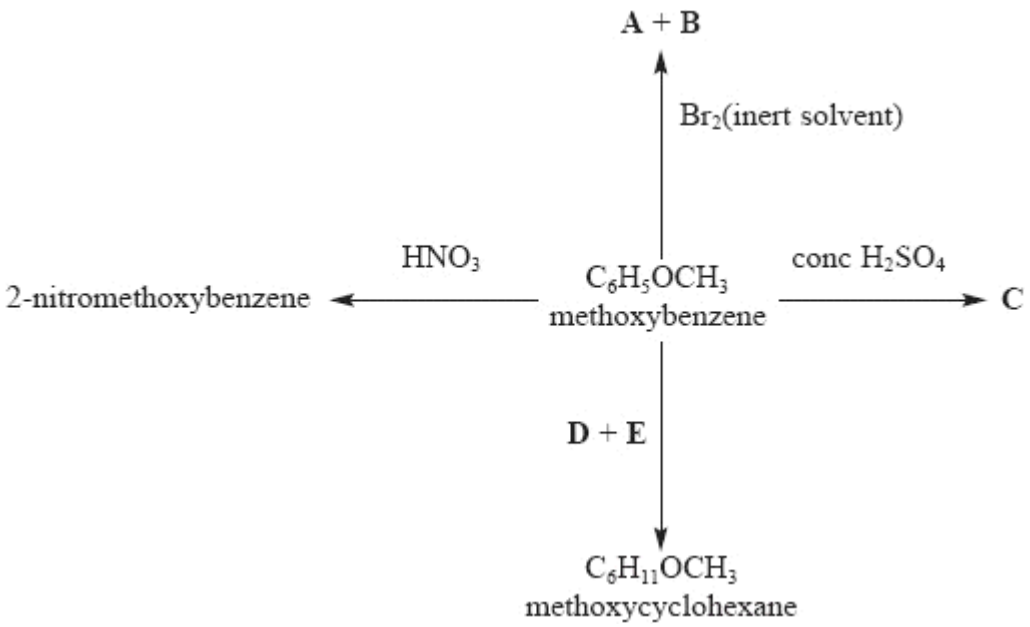
(4)
(Total 16 marks)

6. This question is about the reactions of methoxybenzene, which are summarised in the following diagram.



(a) Draw the fully **displayed** formula for methoxybenzene.

(1)

(b) Three of the reactions in the diagram are electrophilic substitution reactions.

Explain what is meant by the term **electrophilic substitution**.

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.....

(2)

(c) Draw the **structural** formula for 2-nitromethoxybenzene formed when methoxybenzene reacts with nitric acid.

(1)

(d) Give the **molecular** formulae of two of the products, **A** and **B**, formed when methoxybenzene reacts with bromine in an inert solvent.

A

B

(2)

(e) (i) Suggest the name for the organic product, **C**, formed when methoxybenzene reacts with concentrated sulphuric acid.

.....

(1)

(ii) Suggest ONE use for the class of chemicals to which **C** belongs.

.....

(1)

(f) (i) Name reactant **D** and catalyst **E** needed to make methoxycyclohexane from methoxybenzene.

D .....

E .....

(2)

(ii) This reaction is **not** a substitution reaction.

Give TWO alternative names which do describe this type of reaction.

.....

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(2)

(g) Many arenes like methoxybenzene are made from benzene.

(i) What is the natural resource from which benzene is produced?

.....

(1)

(ii) Suggest why methoxybenzene rather than benzene is used in schools and colleges.

.....

(1)

(Total 14 marks)

7. (a) Benzene can be converted into nitrobenzene.

(i) Give the reagents for the reaction.

.....

.....

(2)

(ii) Write the mechanism for the reaction, including the formation of the species that attacks the benzene molecule.

(4)

(iii) Name the type of mechanism involved in this reaction.

.....

(1)

(b) Further reaction produces trinitrobenzene. Draw the structural formulae of the three isomeric trinitrobenzenes.

(3)

(c) Give the reagents and conditions required for the conversion of nitrobenzene into phenylamine, $C_6H_5NH_2$.

.....

.....

(2)

(d) (i) Draw the structural formula of the organic product of the reaction between phenylamine and ethanoyl chloride, CH_3COCl.

(1)

(ii) The organic product of the reaction in (d) (i) is a solid at room temperature. An impure sample of the solid can be purified by recrystallisation. Describe how this recrystallisation can be carried out.

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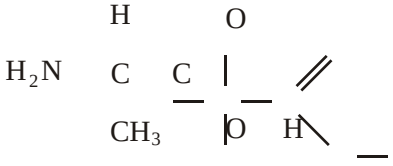
(6)
(Total 19 marks)

8. Alanine, 2-aminopropanoic acid, is the simplest chiral amino acid found in nature and is optically active.



(a) (i) Explain the meaning of the term **chiral**.

.....

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(1)

(ii) How is optical activity detected experimentally?

.....

.....

(2)

(iii) If alanine is made from propanoic acid the product mixture does not show optical activity. Explain why this is so.

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(2)

(b) Alanine reacts with both acids and bases. Give the structural formulae of the compounds you would expect if alanine reacts with

hydrochloric acid

sodium hydroxide

(2)

(c) Alanine has a high melting temperature of 300 °C, much higher than would be expected for the structure given at the start of the question.

Draw the structure that is actually present in the solid, and explain why the melting temperature is so high.

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(2)

(d) Polyamides are made from a diacid dichloride and a diamine; they are condensation polymers.

(i) Explain the term **condensation** polymer.

.....

.....

(1)

(ii) Suggest the structural formula of a diacid dichloride and a diamine that could be reacted to form a polyamide.

(2)

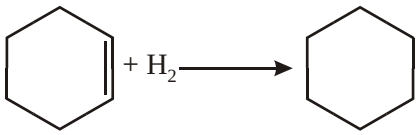
(iii) Draw sufficient of the polymer chain that would result from the reaction of the compounds in (ii) to make the structure of the polymer clear.

(2)

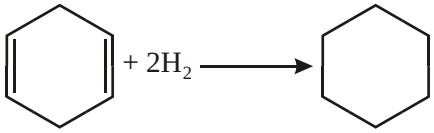
(iv) Alanine could be converted to $CH_3CH(NH_2)COCl$ which on its own could polymerise to a polyamide. Draw the structure of the polymer chain showing three alanine repeating units and all the bonds in the amide links.

(2)
(Total 16 marks)

9. (a) The enthalpy of hydrogenation of cyclohexene is –120 kJ mol^{-1}.



(i) Predict the value of ΔH for the reaction:



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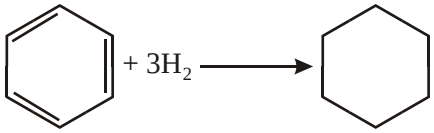
(1)

(ii) Suggest the value of ΔH for the hydrogenation of the hypothetical molecule 1,3,5-cyclohexatriene:



.....

(1)

(iii) The enthalpy of hydrogenation of benzene is –208 kJ mol^{-1}. Explain in terms of the structure and bonding in benzene why this value is different from your answer to (a)(ii).

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(3)

(b) Benzene, C_6H_6, reacts with bromine to form bromobenzene, C_6H_5Br, and hydrogen bromide.

(i) Give the formula of the catalyst that is needed for the reaction.

.....

(1)

(ii) Give the mechanism for the reaction, making clear the role of the catalyst.

(4)

(iii) State the type of mechanism that is commonly found with reactions of benzene and its derivatives.

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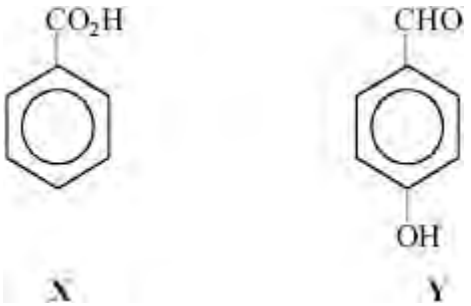
(1)
(Total 11 marks)

10. **X** and **Y** are isomers with the molecular formula $C_7H_6O_2$.



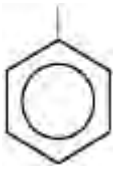
(a) Complete the table with the **observations** you would make when separate samples of **X** and **Y** are warmed gently in test-tubes with the following solutions.

Solution	Observation with **X**	Observation with **Y**
sodium carbonate		
Brady's reagent (2,4-dinitrophenylhydrazine)		
potassium dichromate(VI) + sulphuric acid		

(6)

(b) Both **X** and **Y** can take part in reactions in which esters are formed.

(i) Complete the structural formula of the ester which forms when **X** reacts with methanol.



(1)

(ii) **Y** reacts with ethanoyl chloride to form an ester.

Draw the displayed formula of ethanoyl chloride.

(1)

(iii) Complete the displayed formula of the ester which forms when **Y** reacts with ethanoyl chloride.

(2)

(iv) When **X** forms an ester with methanol, a catalyst is needed for the reaction to proceed at a reasonable speed when heated gently.

Name a suitable catalyst for the esterification reaction.

.....

(1)

(v) Explain why ethanoyl chloride is reactive enough to form an ester with **Y** at a reasonable speed without a catalyst and without heating.

.....

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.....

(2)

(c) The benzene ring in **Y** reacts readily with bromine in a substitution reaction.

(i) Name the **type** of reagent which attacks a benzene ring in substitution reactions.

.....

(1)

(ii) Give the formula of the species which attacks the benzene ring when it reacts with bromine in a substitution reaction.

.....

(1)

(iii) Suggest a structural formula for an organic product of the reaction of bromine with **Y**.

(1)

(iv) **Y** reacts with bromine more readily than benzene does. Suggest a reason for this.

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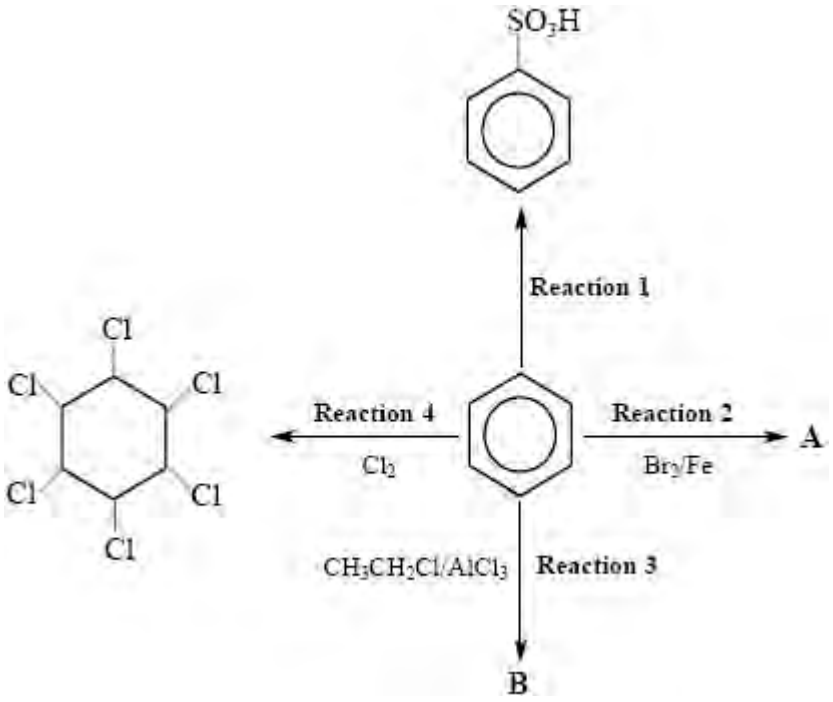
(1)

(Total 17 marks)

11. This question is about the reactions of benzene and some related compounds.



(a) (i) Name the reagent and conditions for **Reaction 1**.

Reagent .....

Conditions.....

(2)

(ii) Give the formula of the attacking species in this reaction.

.....

(1)

(b) (i) Give the structural formula of the organic compound **A** formed in **Reaction 2**.

(1)

(ii) State the type of reaction and its mechanism in **Reaction 2**.

Type .....

Mechanism .....

(2)

(iii) Phenol, C_6H_5OH, will react with bromine in a similar way to benzene, but no catalyst is needed. Explain why phenol will react readily with bromine without a catalyst.

.....

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.....

(2)

(c) (i) Give the name of product **B**.

.....

(1)

(ii) Explain how aluminium chloride acts as a catalyst in **Reaction 3**. You may find it helpful to use an equation in your answer.

.....

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(2)

(d) (i) What condition is needed for chlorine to react with benzene in **Reaction 4**?

.....

(1)

(ii) Give the systematic name of the product of **Reaction 4**.

.....

(1)

(Total 13 marks)

12. (a) Give the structural formula of the organic product when phenol is reacted with:

(i) sodium hydroxide solution

(1)

(ii) aqueous bromine

(1)

(iii) ethanoyl chloride.

(1)

(b) An azo dye can be made from benzenediazonium chloride.

(i) State the reagents and conditions needed to make benzenediazonium chloride from phenylamine.

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(3)

(ii) Write an equation, using structural formulae, to show the reaction between benzenediazonium ions and phenol to give the azo dye.

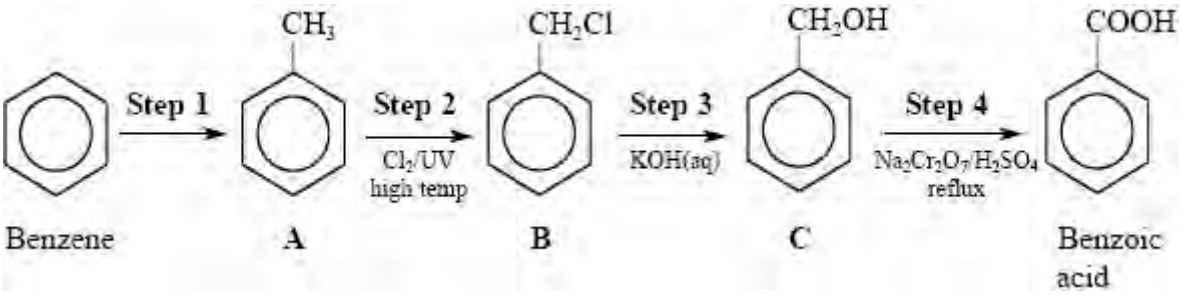
(2)

(iii) What condition is required for the reaction in (ii) above?

.....

(1)
(Total 9 marks)

13. The reaction sequence below shows a method that could be used to convert benzene into benzoic acid.



(a) (i) Name the reagent and catalyst that could be used to convert benzene into **A** in **Step 1**.

Reagent ..... Catalyst .....

(2)

(ii) Name the type of reaction in **Step 1** and its mechanism.

Type ..... Mechanism .....

(2)

(iii) Write an equation to show how the catalyst interacts with the reagent in **Step 1** and explain how this helps the reaction to take place.

Equation

Explanation .....

.....

.....

(2)

(b) (i) **B** has several isomers. Draw the structural formula of ONE of these isomers, and give its systematic name.

Structural formula

Name .....

(2)

(ii) Name the reagent and catalyst you would use to try to make your isomer from **A**.

Reagent ..... Catalyst .....

(2)

(c) (i) Name the type and mechanism of the reaction in **Step 3**.

Type ..... Mechanism .....

(2)

(ii) By considering halogenoalkane **B**, suggest whether the reaction in **Step 3** is first or second order. Justify your answer. Draw formulae to show the mechanism that you suggest.

.....

(2)

(d) What type of reaction is **Step 4**?

.....

(1)

(e) Suggest TWO reactions in which you would observe the same results when carried out with either compound **C** or benzoic acid. Describe what you would **see** in each of the two reactions.

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(4)
(Total 19 marks)

14. (a) A liquid hydrocarbon, **A**, has the molecular formula C_6H_{10}.

A has a boiling point of 356.5 K.

On complete combustion, 4.1 g of **A** forms 7.2 dm^3 of carbon dioxide, and 4.5 g of water.

[Molar volume of a gas is 24 dm^3 under the conditions of the experiment.]

(i) Write the empirical formula of **A** and use the combustion data to show that the empirical formula is correct.

Empirical formula of **A** .....

(3)

(ii) **A** reacts with an excess of bromine water to form **B**, $C_6H_{10}Br_2$. Suggest structural formulae of **A** and **B**.

(2)

(iii) **B** reacts with ammonia to produce **C**, $C_6H_{14}N_2$. Give the structural formula for **C**.

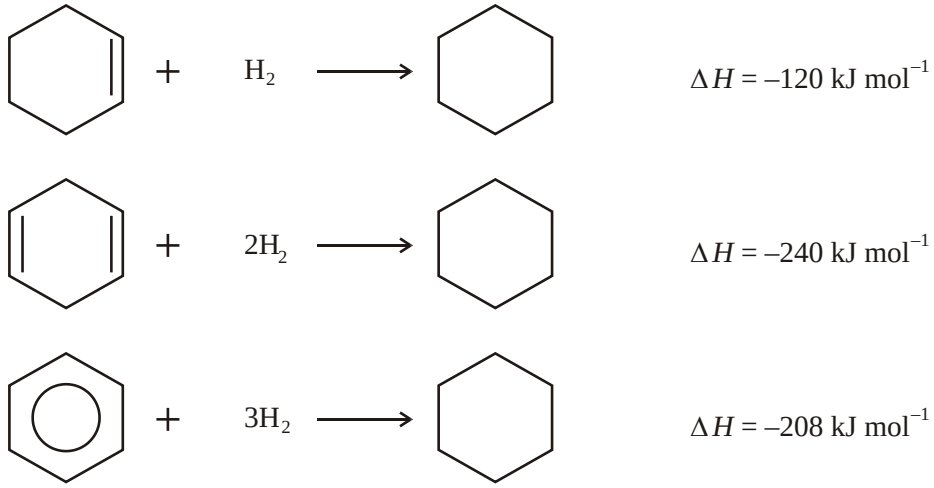
State appropriate conditions, and write the balanced equation, for this reaction.

(4)

(b) Compound **C** reacts with hexanedioyl dichloride to produce a polymer.
Draw the structure of part of the polymer to show TWO repeating units.
State the type of polymerisation involved in making this polymer.

(2)
(Total 11 marks)

15. (a) Equations for the hydrogenation of three compounds are given below, together with the corresponding enthalpy changes.



Explain, in terms of the bonding in benzene, why the enthalpy change of hydrogenation of benzene is **not** –360 kJ mol^{-1}.

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(3)

(b) Benzene can be converted into phenylamine, $C_6H_5NH_2$, in two stages. Give the reagents needed for each step and identify the intermediate compound formed.

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(4)

(c) Benzene, C_6H_6, reacts with bromoethane, CH_3CH_2Br, in the presence of a catalyst, to form ethylbenzene, $C_6H_5CH_2CH_3$, and hydrogen bromide.

(i) Give the formula of a catalyst for this reaction.

.....

(1)

(ii) Give the mechanism for the reaction between benzene and bromoethane, including the formation of the species that reacts with the benzene molecule.

(4)

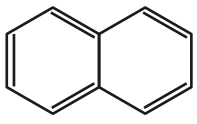
(iii) Name the type of mechanism involved in this reaction.

.....

(1)

(Total 13 marks)

16. This question is about the arene, naphthalene. The structure of naphthalene can be shown as

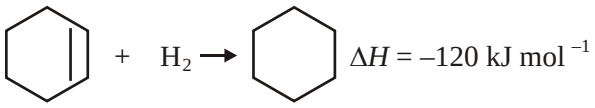


(a) What is the molecular formula of naphthalene?

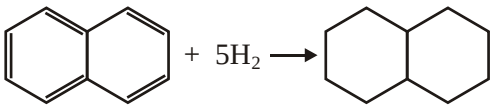
.....

(1)

(b) The enthalpy change, ΔH, for the addition of hydrogen to cyclohexene to form cyclohexane is –120 kJ mol^{-1}.



(i) Calculate the enthalpy change of the hydrogenation reaction shown below.



ΔH = ... kJ mol^{-1}

(1)

(ii) Experimental work shows that ΔH for the hydrogenation of naphthalene is actually –333 kJ mol^{-1}. What does this suggest about the stability and structure of naphthalene?

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(2)

(iii) Would you expect naphthalene to decolorise bromine solution? Justify your answer.

.....

.....

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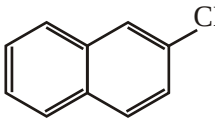
(1)

(c) The Friedel-Crafts reaction enables an alkyl group to be attached to an arene ring.

(i) Suggest the reagent and catalyst you would need to make



from naphthalene.

Reagent .....

Catalyst .....

(2)

(ii) Name the type of reaction and its mechanism.

.....

(2)

(Total 9 marks)

17. (a) (i) Describe the appearance of the organic product obtained when an aqueous solution of bromine is added to aqueous phenol.

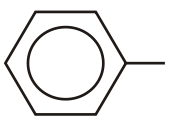
.....

(1)

(ii) Give the equation for the reaction in (a)(i).

(2)

(iii) Phenol reacts with ethanoyl chloride to form an ester. Complete the structural formula to show the ester produced in this reaction.



(1)

(iv) Suggest, in terms of the bonding in ethanoyl chloride, why the reaction in (a)(iii) proceeds without the need for heat or a catalyst.

.....

.....

.....

(2)

(b) Phenylamine, $C_6H_5NH_2$, is formed by the reduction of nitrobenzene, $C_6H_5NO_2$. Give the reagents which are used.

.....

.....

(1)

(c) Phenylamine is used to prepare azo dyes.

(i) State the reagents needed to convert phenylamine into benzenediazonium chloride.

.....

.....

(2)

(ii) The reaction in (c)(i) is carried out at a temperature maintained between 0 °C and 5 °C. Explain why this is so.

.....

.....

.....

.....

(2)

(iii) Addition of benzenediazonium chloride solution to an alkaline solution of phenol gives a precipitate of the brightly coloured dye, 4-hydroxyazobenzene. Give the structural formula of 4-hydroxyazobenzene.

(1)

(iv) Describe how recrystallisation is used to purify a sample of the solid dye formed in (c)(iii).

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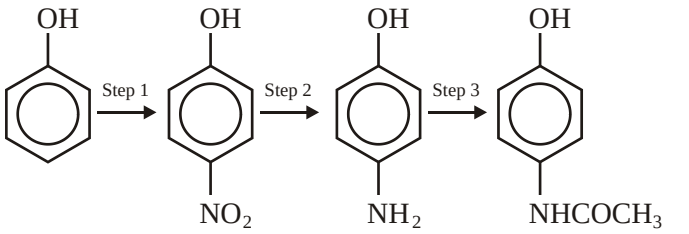
(5)
(Total 17 marks)

18. Paracetamol can be manufactured from phenol using the reaction sequence below.



A **B** **C** **Paracetamol**

(a) Give reagents and conditions for **Step 1**.

.....

.....

(2)

(b) State the type of reaction that occurs in **Step 2**.

.....

(1)

(c) (i) Give the name of compound **C**.

.....

(1)

(ii) Suggest a test and its results for the amino group in compound **C**.

.....

.....

.....

(2)

(d) (i) Write a balanced equation for the reaction occurring when paracetamol is boiled with an aqueous solution of sodium hydroxide.

(2)

(ii) Would you expect paracetamol to react with sodium carbonate solution? Justify your answer.

.....

.....

(1)

(e) (i) Suggest which types of intermolecular forces exist between paracetamol molecules. For each type of force give an example of the parts of the molecules involved.

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(4)

(ii) Suggest a reason why paracetamol is only sparingly soluble in water.

.....

.....

(1)

(f) Suggest which bond gives rise to the broadest absorption in the infrared spectrum of paracetamol.
State the range of wavenumbers for this absorption.

.....

.....

(2)

(g) (i) Give the molecular formula of the ion with the highest molecular mass in the mass spectrum of paracetamol.

.....

(1)

(ii) Suggest the formulae of the ions responsible for the peaks at mass / charge ratios 43 and 93.

.....

.....

.....

.....

(2)

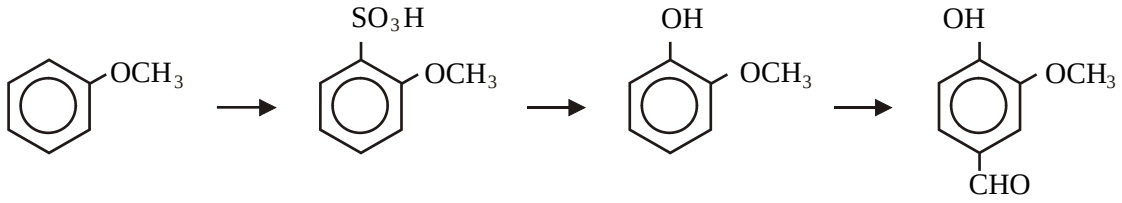
(h) Suggest ONE advantage of using paracetamol, rather than aspirin, as a pain reliever.

.....

.....

(1)
(Total 20 marks)

19. Vanillin, the main ingredient of vanilla essence, is one of the commonest flavouring ingredients found in foods. Synthetic vanillin, which is identical to natural vanillin, can be manufactured from methoxybenzene. One synthetic route is shown below:



methoxybenzene | 2-methoxybenzene sulphonic acid | 2-methoxyphenol | vanillin

(a) (i) Name the reagent which converts methoxybenzene to 2-methoxybenzene sulphonic acid.

.....

(1)

(ii) Name the type of reaction which occurs and its mechanism.

.....

(2)

(b) After the final stage, in which 2-methoxyphenol is converted to vanillin, the impure product can be purified by recrystallisation. In this process the solid is dissolved in the minimum volume of hot water. The mixture is then filtered whilst still hot. The filtrate is cooled in an ice bath to produce crystals of vanillin. These can be removed by filtration and dried.

(i) Why is the “minimum volume of hot water” used?

.....

.....

(1)

(ii) The impure vanillin may contain soluble and insoluble impurities. Describe how each of these is removed during recrystallisation.

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(2)

(iii) How would you check the purity of the vanillin after recrystallisation, other than by using an infrared spectrometer.

.....

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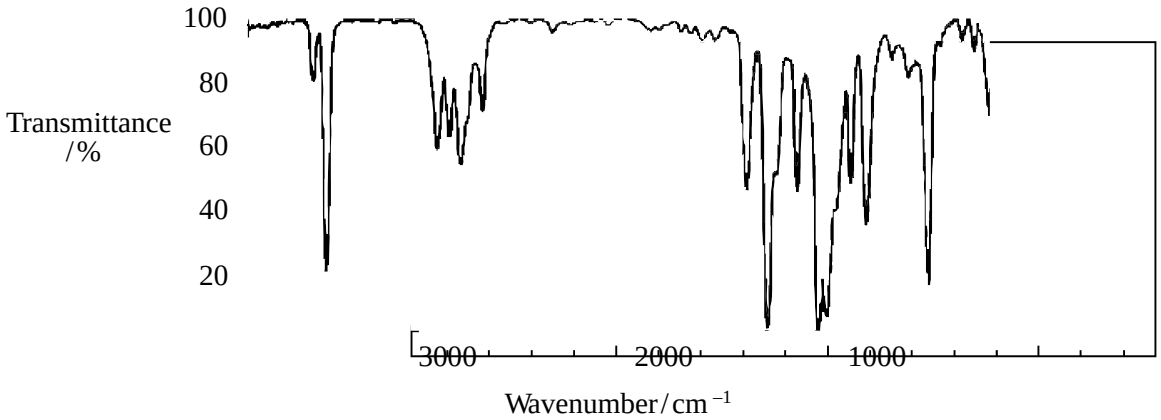
(2)

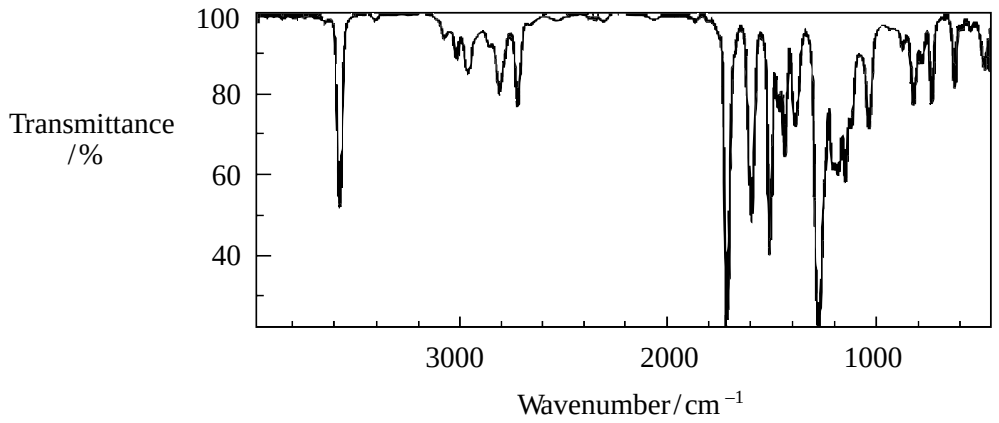
(c) In order to establish whether or not vanillin had been formed, two infrared spectra were obtained: a sample of pure 2-methoxyphenol and a sample of the product.

Study the spectra and data below.

Infrared Spectrum of 2-Methoxyphenol



Infrared Spectrum of Product



		Wavenumber / cm^{-1}
C═C Stretching Vibrations	Arene	1600 – 1450
C—H Stretching Vibrations	Arene	3030
O—H Stretching Vibrations	Alcohols and phenols	3750 – 3200
C═O Stretching Vibrations	Aldehydes Ketones Carboxylic acids Esters	1740 – 1720 1700 – 1680 1725 – 1680 1750 – 1735

Comment as to whether any vanillin is likely to have been formed during the process. Support your answer with relevant evidence.

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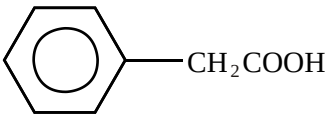
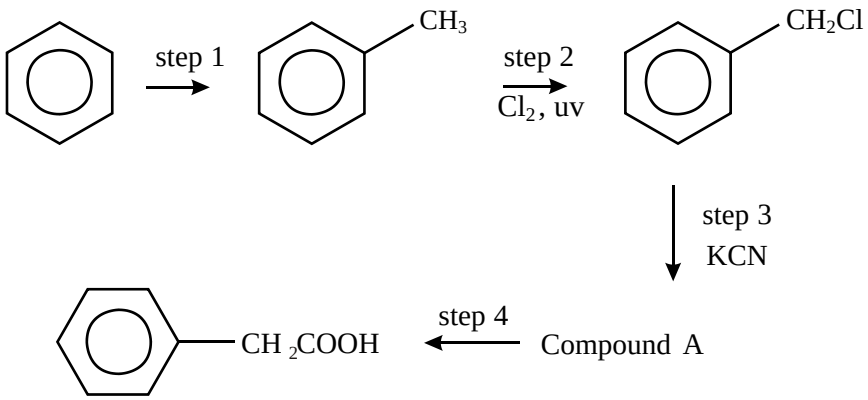
.....

(2)
(Total 10 marks)

20. Phenylethanoic acid occurs naturally in honey as its ethyl ester: it is the main cause of the honey's smell.

The acid has the structure 

Phenylethanoic acid can be synthesised from benzene as follows:



(a) State the reagent and catalyst needed for **step 1**.

.....

.....

(2)

(b) (i) What **type** of reaction is **step 2**?

.....

(1)

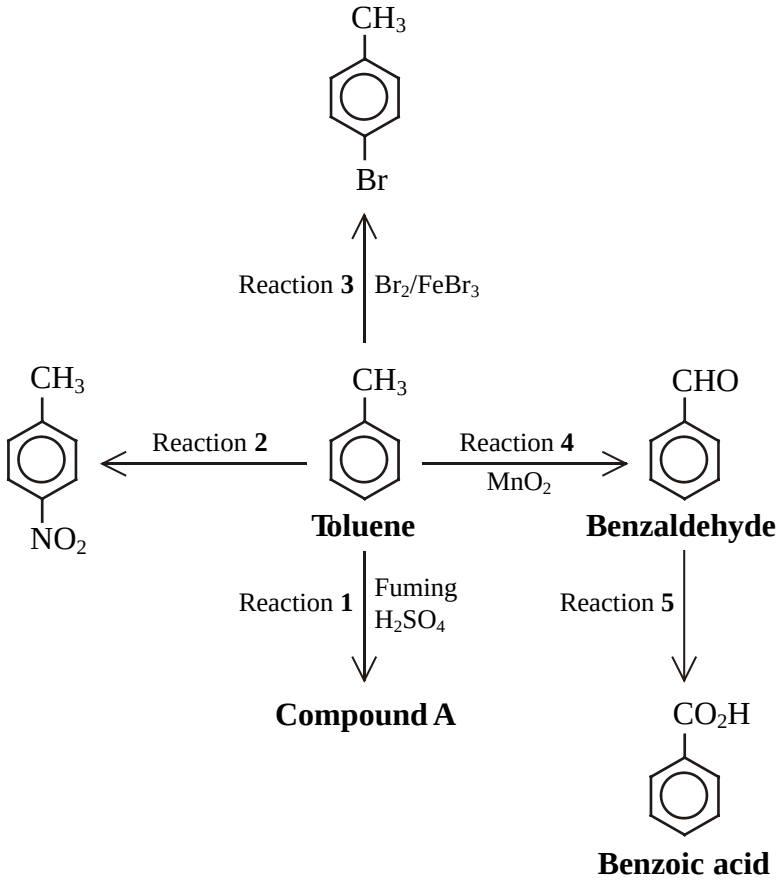
(ii) Suggest a mechanism for **step 2**. You should include the initiation step, the two propagation steps and a termination step.
You may use Ph to represent the phenyl group, C_6H_5.

(4)

(iii) Draw an apparatus which would enable you to carry out **step 2**, in which chlorine is bubbled through boiling methylbenzene, safely.
Do **not** show the uv light source.

(3)
(Total 10 marks)

21. Toluene is the non-systematic name of an arene widely used in industry. Its formula is $C_6H_5CH_3$. Some of its reactions are summarised in the following diagram.



(a) (i) Give the systematic name of toluene.

.....

(1)

(ii) Draw a possible structural formula for **compound A**.

(1)

(b) (i) Name the TWO reagents needed for Reaction **2**.

.....

.....

(2)

(ii) Give the formula of the attacking species in Reaction **2**.

.....

(1)

(c) (i) Give the reaction type and mechanism in Reaction **3**.

Reaction Type

.....

Mechanism

.....

(2)

(ii) Suggest why Reactions 1, 2 and 3 all take place under milder conditions than similar reactions involving benzene.

.....

.....

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.....

.....

.....

(2)

(d) What type of reaction does toluene undergo in Reaction **4**?

.....

(1)

(e) Name the TWO reagents needed for Reaction **5**.

.....

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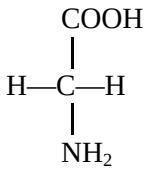
(2)

(Total 12 marks)

22. (a) Glycine is an amino acid.



(i) Draw the full structural formula of the zwitterion of glycine, showing **all** bonds.

(1)

(ii) Explain how the zwitterion in glycine is formed.

.....

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.....

(1)

(iii) Use your answer to (i) to explain why glycine has a high melting temperature of 262 °C.

.....

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(2)

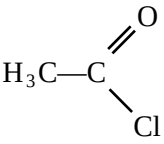
(b) Suggest the formula of the organic product formed when glycine reacts, under suitable conditions, with

(i) hydrogen ions, H^+

(1)

(ii) hydroxide ions, OH^-

(1)

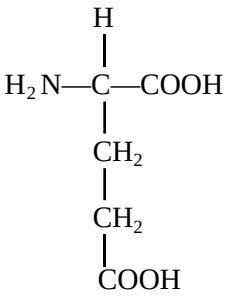
(iii) ethanoyl chloride, 

(1)

(iv) methanol, CH_3OH

(1)

(c) Glutamic acid is also an amino acid. The formula of glutamic acid is shown below.



Glutamic acid exists as two optical isomers whereas glycine does not.

(i) Why is glutamic acid chiral?

.....

.....

.....

(1)

(ii) How can the two optical isomers of glutamic acid be distinguished from each other?

.....

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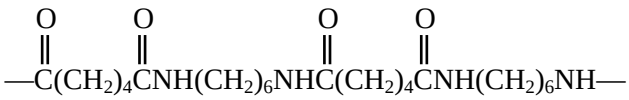
.....

(2)

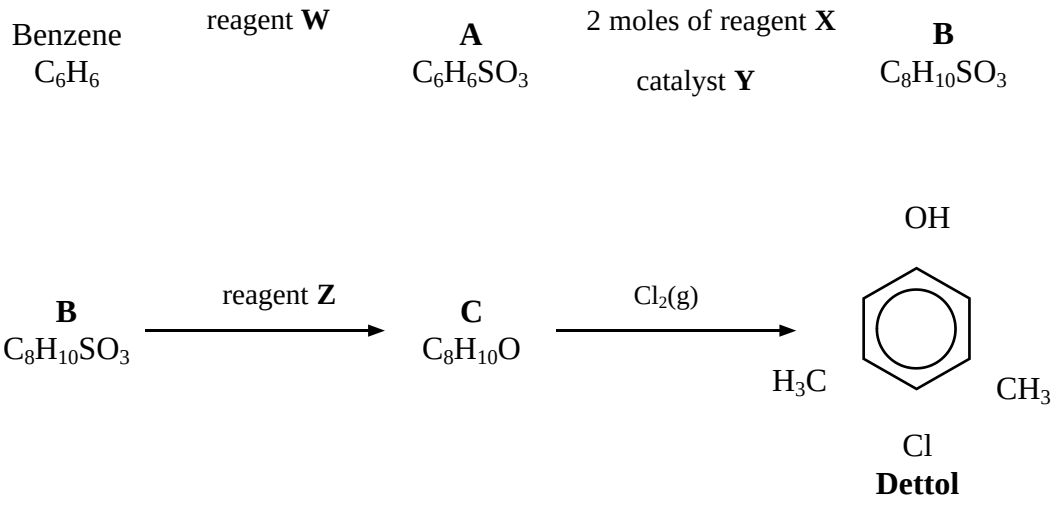
(d) A section of the polymer nylon-6,6 is shown below



Give the formulae of TWO monomers which could react together, under suitable conditions, to form nylon-6,6.

(2)
(Total 13 marks)

23. The reaction scheme below shows a synthesis of the antiseptic, Dettol, from benzene.



Study this reaction scheme carefully before answering any of the questions below.

(a) (i) Give the structural formula of **A**.

(1)

(ii) Name reagent **W**.

.....

(1)

(iii) State the type of reaction and the mechanism for the conversion of benzene into **A**.

.....

(1)

(iv) Give the **formula** of the species which attacks benzene to form **A**.

.....

(1)

(b) (i) Suggest the structural formula of **B**. You may find it helpful to study the formula for Dettol, as well as your answer to (a)(i), when answering this question.

(1)

(ii) Give the formulae for reagent **X** and catalyst **Y**.

Reagent **X** ..... Catalyst **Y** .....

(2)

(iii) What gaseous inorganic compound will also be produced during the formation of **B**?

.....

(1)

(c) (i) Give the systematic name for Dettol.

.....

(1)

(ii) Suggest why Dettol does not mix well with water.

.....

.....

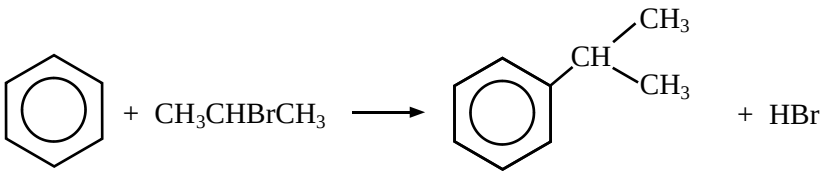
.....

.....

(1)

(Total 10 marks)

24. (a) Benzene reacts with 2-bromopropane in a Friedel-Crafts reaction to give 2-phenylpropane, $C_6H_5CH(CH_3)_2$, usually known as cumene.



cumene

Cumene is used to manufacture phenol and propanone.

(i) Identify a suitable catalyst for the reaction between benzene and 2-bromopropane.

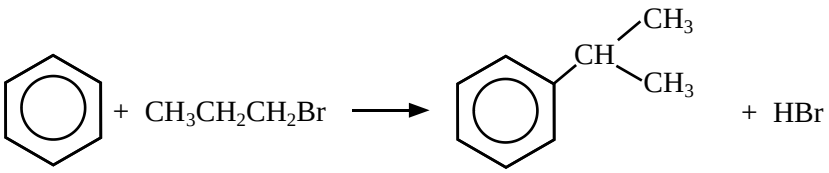
.....

(1)

(ii) Give the mechanism for the reaction, including the formation of the electrophile.

(4)

(b) If benzene and 1-bromopropane, $CH_3CH_2CH_2Br$, are reacted under similar conditions to those in part (a), the product is still cumene although 1-phenylpropane $C_6H_5CH_2CH_2CH_3$ might have been the expected product.



cumene

(i) Draw the structure of the carbocation which would initially be formed.

(1)

(ii) Suggest, in terms of relative stabilities of carbocations, what happens to the carbocation in (i) which results in cumene as the product of the reaction rather than 1-phenylpropane.

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.....

(2)

(c) Phenol reacts with the benzenediazonium cation, $C_6H_5N_2^+$, in alkaline conditions to give an azo dye.

(i) State the reagents needed to convert phenylamine into a solution containing $C_6H_5N_2^+$ ions.

.....

(2)

(ii) Explain why the temperature of the reaction in (c)(i) needs to be kept between 0 °C and 10 °C.

.....

.....

.....

(2)

(iii) Give the structural formula of the **product** from the reaction between benzenediazonium chloride and phenol.

(2)

(d) (i) How would you show that propanone is a carbonyl compound **and** is a ketone, not an aldehyde?

.....

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(3)

(ii) A characteristic reaction of the carbonyl group, C═O, is nucleophilic addition. The C═C double bond reacts by electrophilic addition.

Suggest the reason for the difference.

.....

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.....

(2)

(iii) Give the mechanism for the nucleophilic addition reaction between propanone and hydrogen cyanide in the presence of a catalyst of cyanide ions, CN^-.

(3)
(Total 22 marks)

25. (a) The conversion of butan-2-ol to 2-bromobutane can be performed as outlined below:

- Butan-2-ol is heated with a mixture of 50 % aqueous sulphuric acid and sodium bromide for 45 minutes.
- The crude 2-bromobutane is distilled off.
- The crude 2-bromobutane is shaken with pure water, which removes the sulphuric acid and some of the butan-2-ol that contaminates the product.
- The organic layer is separated and then shaken with concentrated hydrochloric acid to remove residual butan-2-ol.
- The organic layer is then shaken with dilute sodium carbonate solution.
- Anhydrous calcium chloride is added to the organic layer and allowed to stand for some hours.
- The organic layer is then redistilled in a dry apparatus.

(i) Explain, in terms of kinetic factors, why the mixture is heated for a significant amount of time.

.....

.....

(1)

(ii) Why is sulphuric acid necessary in the reaction mixture?

.....

.....

.....

(2)

(iii) Suggest why butan-2-ol, which is only partially miscible with water, is much more soluble in concentrated hydrochloric acid.

.....

.....

.....

.....

(2)

(iv) Why is the organic layer shaken with dilute sodium carbonate solution?

.....

.....

(1)

(v) What is the purpose of the anhydrous calcium chloride?

.....

(1)

(vi) How would you heat the mixture safely? Explain your choice of method.

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.....

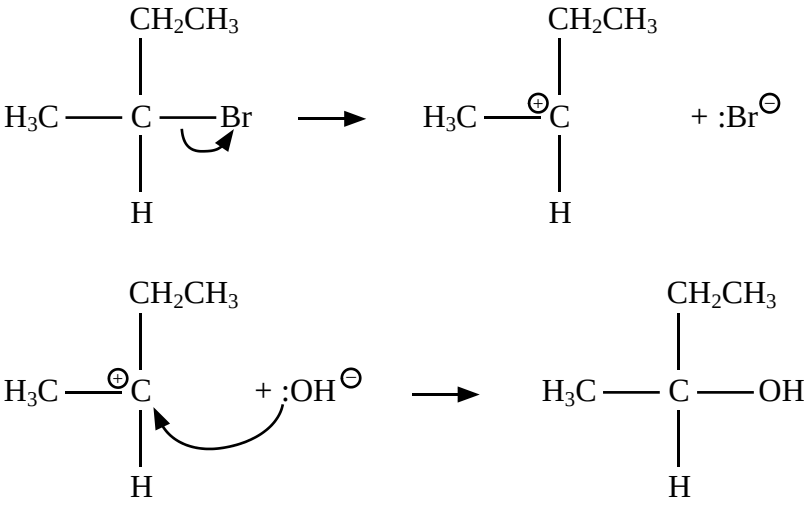
(2)

(b) Both 2-bromobutane and butan-2-ol are chiral molecules.

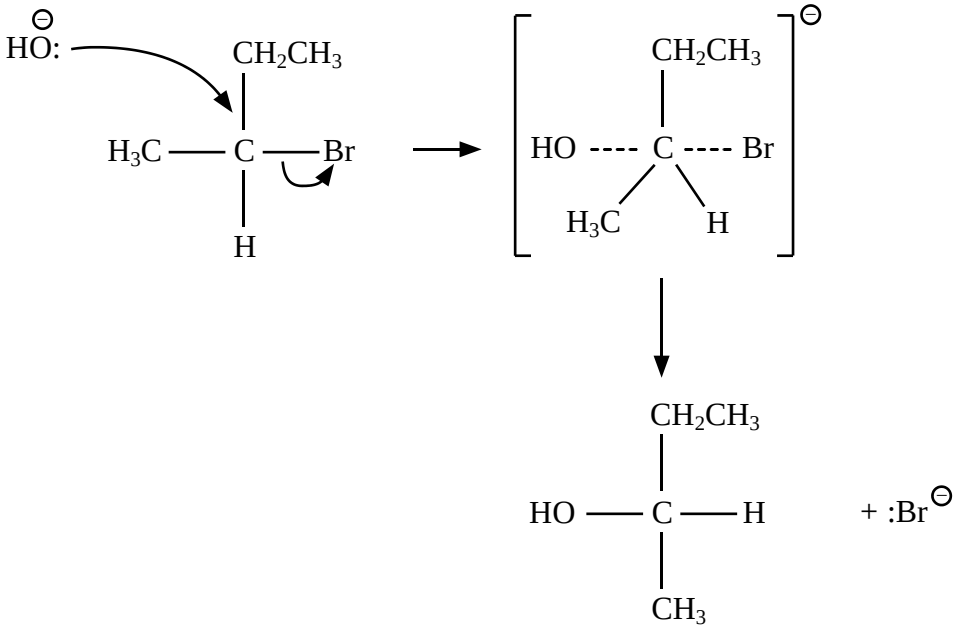
If one optical isomer of 2-bromobutane is used to make butan-2-ol by reaction with aqueous hydroxide ions, the product mixture is **not** optically active.

The mechanism for the reaction is either S_N1 or S_N2; these are given below

S_N1



S_N2



Explain which one of these mechanisms is consistent with the lack of optical activity in the product mixture.

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(3)

(c) The oxidation of butan-2-ol with hot potassium dichromate(VI) in acidic solution produces butanone, $CH_3COCH_2CH_3$.

(i) What would you **see** as the reaction proceeds?

.....

(1)

(ii) The dichromate(VI) ion is reduced under these conditions to chromium(III) ions.

The half-equation for the oxidation of butan-2-ol to butanone is

$$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e^-$$

Write the ionic half-equation for the reduction of dichromate(VI) ions, and hence derive the overall equation for the oxidation of butan-2-ol.

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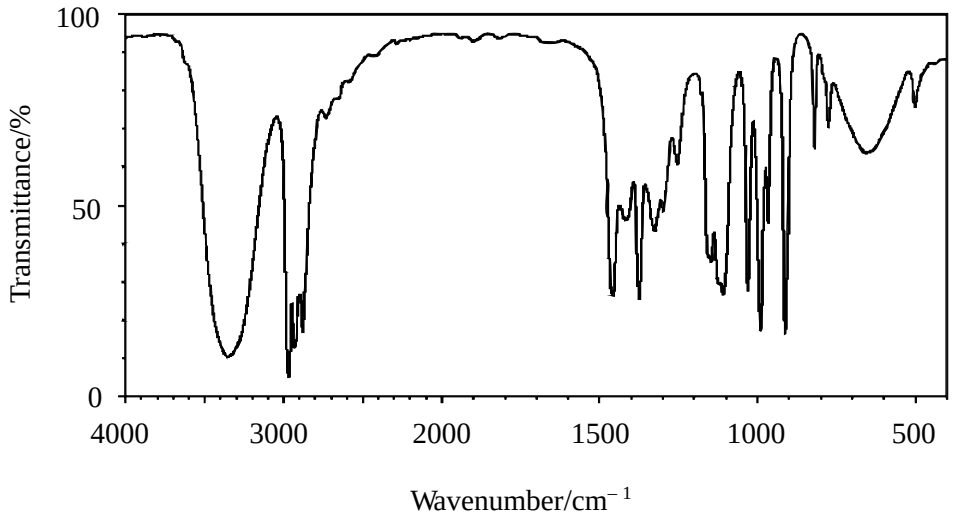
.....

.....

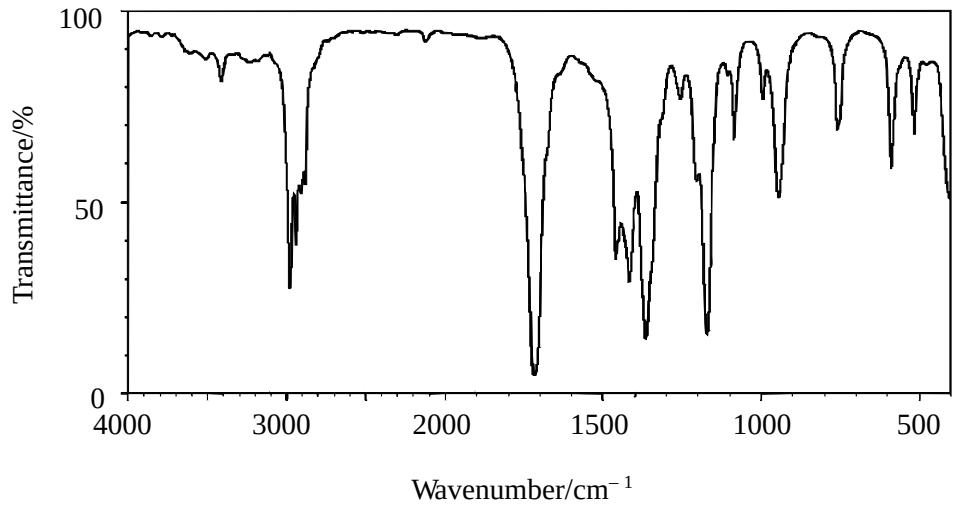
(2)

(iii) The IR spectra of butan-2-ol and of the organic product from its oxidation with dichromate(VI) ions are given below.

Spectrum of butan-2-ol



Spectrum of the organic product from the oxidation of butan-2-ol



Bond	Wavenumber/cm^{-1}	Bond	Wavenumber/cm^{-1}
C—H (alkanes)	2850–3000	C—O (alcohols, esters)	1000–1300
C—H (alkenes)	3000–3100	O—H (hydrogen-bonded alcohols)	3230–3550
C=O (aldehydes, ketones, carboxylic acids)	1680–1750	O—H (hydrogen-bonded carboxylic acids)	2500–3300

What evidence is there from the spectra that the reaction in part (ii) has occurred?

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(2)

(d) When potassium dichromate(VI) is dissolved in water, the following equilibrium is set up

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

(i) If a solution of barium ions is then added to **this solution**, solid barium chromate, $BaCrO_4$, is precipitated; it is sparingly soluble in water, so the equilibrium given below also exists in the solution

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons BaCrO_4(s)$$

Explain what happens to the pH when the barium ions are added.

.....

.....

.....

.....

(2)

(ii) If a solution of lead(II) ions is added instead of barium ions, solid $PbCrO_4$ is precipitated. This is almost completely insoluble in water so all chromate(VI) ions are removed from solution

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

State how the pH of this solution differs from your answer in part (i).

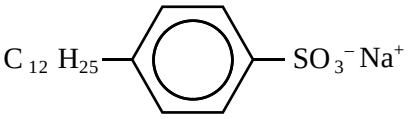
.....

.....

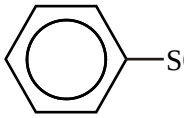
(1)

(Total 20 marks)

26. An important industrial compound, **S**, has the formula



(a) (i) Name the reagents and give the conditions where necessary for the two steps needed to make



from benzene.

Step 1 Reagent .....

Conditions .....

Step 2 Reagent .....

(3)

(ii) Name the type of reaction in each step.

Step 1 .....

Step 2 .....

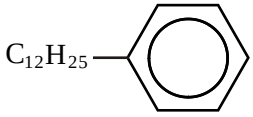
(2)

(b) (i) What is the specific name given to the reaction when an alkyl group is introduced into the benzene ring by electrophilic substitution?

.....

(1)

(ii) Give the molecular formula of the reagent and of the catalyst needed to make



from benzene.

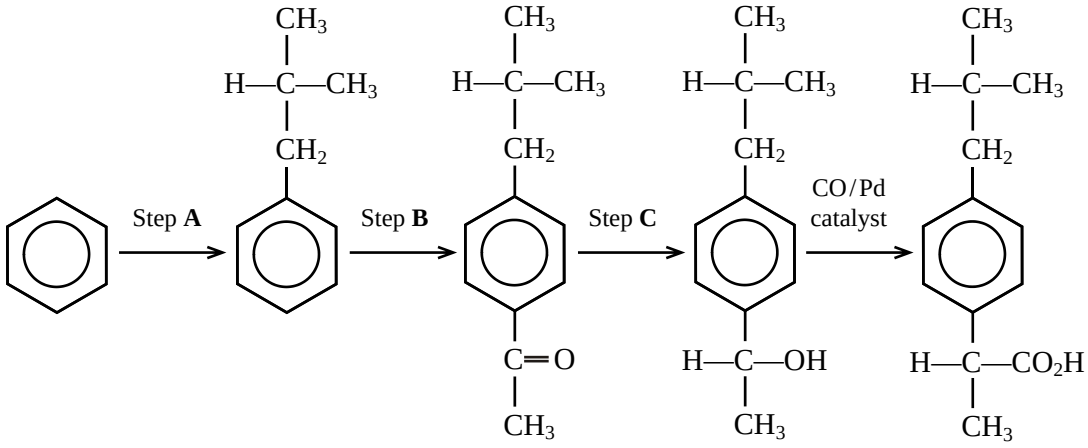
Reagent .....

Catalyst .....

(2)

(Total 8 marks)

27. The drug ibuprofen can be synthesised from benzene by the route shown below.



Ibuprofen

(a) Name the type and mechanism of the reaction in Step **A**, and suggest a suitable reagent and catalyst.

Type and mechanism .....

Name of the reagent for Step **A** .....

Catalyst .....

(3)

(b) Step **C** is a reduction.

Give ONE reason why lithium tetrahydridoaluminate, $LiAlH_4$, is preferred to hydrogen as a reducing agent in this reaction.

.....

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.....

(2)

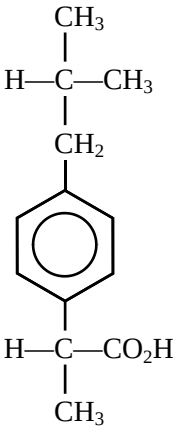
(c) A sample of the final product was analysed by combustion. 1.00 g was burnt in oxygen. It produced 2.78 g carbon dioxide and 0.786 g water.

State the molecular formula of ibuprofen and show that these results are consistent with it.

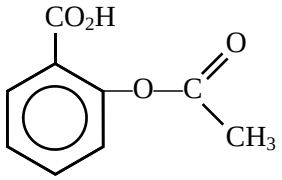
(4)

(d) Ibuprofen can be analysed by instrumental methods. The infrared spectra of ibuprofen and two other drugs, aspirin and paracetamol, not necessarily in that order, are shown opposite.

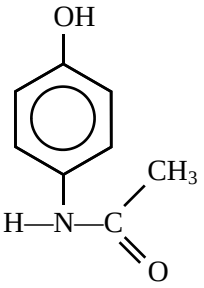
Ibuprofen has the formula



Aspirin has the formula



Paracetamol has the formula



(i) Explain, referring to the structure of each molecule, why infrared spectroscopy is **not** a good technique to distinguish aspirin from ibuprofen.

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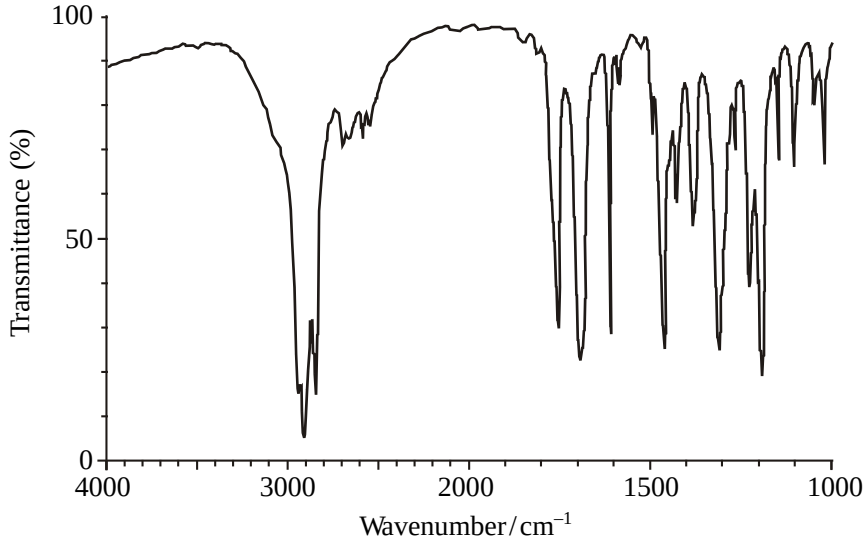
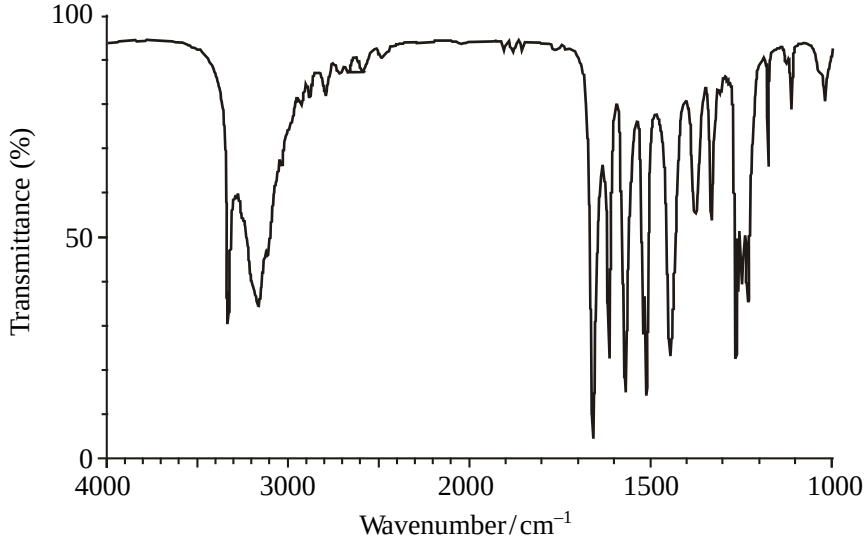
(1)

(ii) Deduce which of **X**, **Y** or **Z** is the infrared spectrum of paracetamol, giving a piece of evidence from the spectrum you select.

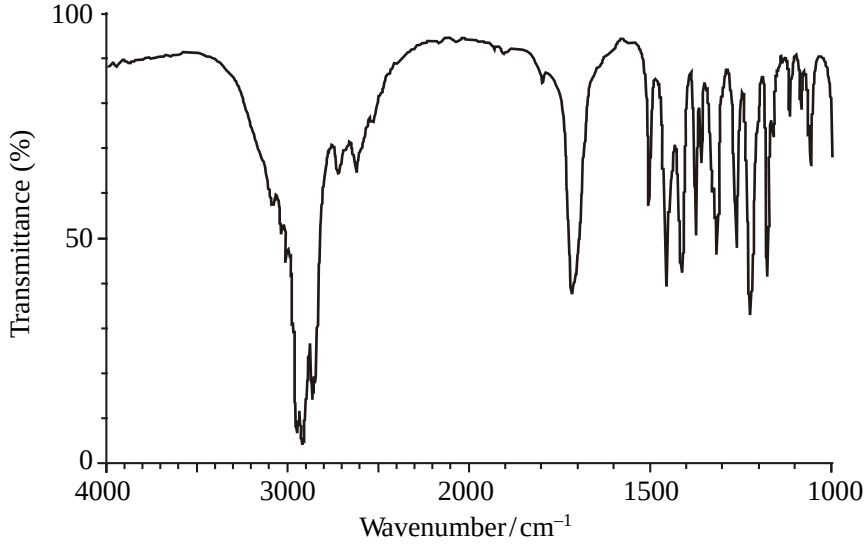
Spectrum X



Spectrum Y



Spectrum Z



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(1)

(iii) Ibuprofen and aspirin can be distinguished using their mass spectra.

A line at mass/charge ratio 57 occurs only in the mass spectrum of ibuprofen. Give the formula of the ion which produces this line.

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Suggest the mass/charge ratio of one line which occurs in the mass spectrum of aspirin but **not** ibuprofen, and the formula of the species which produces it.

.....

.....

(3)
(Total 14 marks)

28. **X**, **Y**, and **Z** are three different compounds from the list below. **X** and **Y** react together to form an ester. **X** and **Z** also react to give the same ester as **X** and **Y**, but less readily.

Compound **Y** could be

A propanoyl chloride

B propanoic acid

C propan-1-ol

D propanal

(Total 1 mark)

29. Which of the following isomers of $C_4H_{10}O$ has a chiral centre?

A Butan-1-ol

B Butan-2-ol

C 2-methylpropan-1-ol

D 2-methylpropan-2-ol

(Total 1 mark)

30. When the colourless liquid chlorobenzene is shaken with bromine water, the chlorobenzene becomes a yellow orange colour. What is the interpretation of this?

A an addition compound of chlorobenzene and bromine has formed.

B the chlorine atom has been replaced by a bromine atom.

C a hydrogen atom has been replaced by a bromine atom.

D the bromine is more soluble in chlorobenzene than in water.

(Total 1 mark)

31. What class of organic compound has a characteristic smell and gives a solution in water with a pH of about 10?

A arene

B amine

C aldehyde

D carboxylic acid

(Total 1 mark)

32. The substance of formula $(OCH_2CH_2OOCC_6H_4COOCH_2CH_2OOCC_6H_4CO)_n$ is a

A polyester

B natural oil or fat

C detergent

D protein

(Total 1 mark)

33. The optical isomers of alanine, $CH_3CH(COOH)NH_2$

A have different melting points

B rotate the plane of plane polarised light in opposite directions

C react at different rates with ethanoyl chloride, CH_3COCl

D both occur naturally in protein molecules

(Total 1 mark)

34. The rate equation for the reaction between aqueous sodium hydroxide and 2-chloro-2-methylpropane is

Rate = k[2-chloro-2-methylpropane]

The first step in the mechanism of this substitution reaction is

A nucleophilic attack by OH^- ions on the carbon atom in the C–Cl bond

B electrophilic attack by OH^- ions on the carbon atom in the C–Cl bond

C the breaking of the C–Cl bond to form a carbocation

D the simultaneous making of a O–C bond as the C–Cl bond breaks

(Total 1 mark)

35. When hydrogen cyanide, HCN, is added to ethanal, CH_3CHO, the resulting solution has no effect on the plane of polarisation of plane polarised light.

This is because

A ethanal is not chiral

B the product is not chiral

C the intermediate is planar

D the product is a racemic mixture

(Total 1 mark)

36. This question is about the following organic compounds:

A Benzene, C_6H_6

B Glycine, NH_2CH_2COOH

C Propene, CH_3CHCH_2

D Propanone, CH_3COCH_3

Select, from **A–D**, the compound which would

(a) be a solid at room temperature

A

B

C

D

(1)

(b) give a salt by reaction with sodium hydroxide

A

B

C

D

(1)

(c) give a sulfonic acid by reaction with fuming sulfuric acid

A

B

C

D

(1)

(d) form a precipitate when reacted with 2,4-dinitrophenylhydrazine

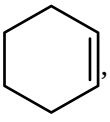
A

B

C

D

(1)
(Total 4 marks)

37. (a) (i) Write the equation for the reaction between cyclohexene,  , and bromine.

(1)

(ii) Draw out the mechanism for this reaction.

(3)

(b) (i) Write the equation for the reaction between benzene,  , and bromine in the presence of a catalyst of anhydrous iron(III) bromide, $FeBr_3$.

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(1)

(ii) Draw out the mechanism for this reaction. Include an equation for the formation of the species that attacks the benzene ring.

(4)

(iii) Write an equation to show how the catalyst is regenerated.

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(1)

(c) Comment critically on:

(i) the differences and similarities of the first steps involving the organic compounds in both reactions.

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(3)

(ii) why the two intermediates formed in these first steps then react differently?

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(3)

(d) State the number of peaks in the proton nmr spectrum of the **product** of the reaction between cyclohexene and bromine.

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(1)

(Total 17 marks)