AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



EXAM QUESTION PACK

3.3.9 CARBOXYLIC ACIDS AND DERIVATIVES

SCORE	PERCENTAGE
/379	%

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Q1.

Acyl chlorides are useful reagents in synthesis. They react with aromatic compounds and also with alcohols.

(a) CH_3CH_2COCl reacts with benzene in the presence of $AlCl_3$ in an electrophilic substitution reaction.

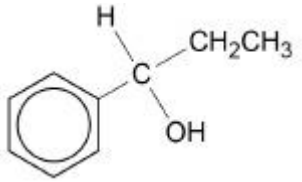
Give an equation for the reaction of CH_3CH_2COCl with $AlCl_3$ to form the electrophile.
Outline a mechanism for the reaction of this electrophile with benzene.

Equation _____

Mechanism

(4)

(b) The organic product in **part (a)** can be converted into the alcohol shown.



Give the IUPAC name of the alcohol.
Give the reagent needed for this reaction and name the mechanism.

IUPAC name _____

Reagent _____

Name of mechanism _____

(3)

(c) The alcohol shown in **part (b)** reacts with ethanoyl chloride to form an ester.

Describe what would be observed when the alcohol reacts with ethanoyl chloride.
Name the mechanism for the reaction to form the ester.
Draw the structure of the ester.

Observation _____

_____

Name of mechanism _____

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Structure of ester

(3)
(Total 10 marks)

Q2.

Use the Data Booklet to help you answer this question.

This question is about amino acids and peptide (amide) links.

(a) Draw the structure of the zwitterion formed by phenylalanine.

(1)

(b) Draw the structure of serine at high pH.

(1)

(c) Draw the structures of both dipeptides formed when phenylalanine reacts with serine.

In each structure show all the atoms and bonds in the amide link.

(2)

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(d) An amide link is also formed when an acyl chloride reacts with a primary amine.

Name and outline a mechanism for the reaction between CH_3CH_2COCl and $CH_3CH_2NH_2$

Give the IUPAC name of the organic product.

Name of mechanism _____

Mechanism

IUPAC name of organic product _____

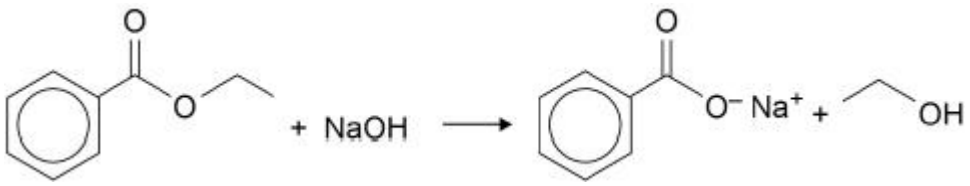
(6)

(Total 10 marks)

Q3.

Benzoic acid can be prepared from ethyl benzoate.

Ethyl benzoate is first hydrolysed in alkaline conditions as shown:



A student used the following method.

Add 5.0 cm^3 of ethyl benzoate (density = 1.05 g cm^{-3}, M_r = 150) to 30.0 cm^3 of aqueous 2 mol dm^{-3} sodium hydroxide in a round-bottomed flask.

Add a few anti-bumping granules and attach a condenser to the flask. Heat the mixture under reflux for half an hour. Allow the mixture to cool to room temperature.

Pour 50.0 cm^3 of 2 mol dm^{-3} hydrochloric acid into the cooled mixture.

Filter off the precipitate of benzoic acid under reduced pressure.

(a) Suggest how the anti-bumping granules prevent bumping during reflux.

_____

_____

_____

(1)

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(b) Show, by calculation, that an excess of sodium hydroxide is used in this reaction.

(2)

(c) Suggest why an excess of sodium hydroxide is used.

_____

_____

(1)

(d) Suggest why an electric heater is used rather than a Bunsen burner in this hydrolysis.

_____

_____

(1)

(e) State why reflux is used in this hydrolysis.

_____

_____

(1)

(f) Write an equation for the reaction between sodium benzoate and hydrochloric acid.

_____

(1)

(g) Suggest why sodium benzoate is soluble in cold water but benzoic acid is insoluble in cold water.

_____

_____

_____

_____

_____

(2)

(h) After the solid benzoic acid has been filtered off, it can be purified.

Describe the method that the student should use to purify the benzoic acid.

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_____

_____

_____

_____

_____

_____

_____

_____

(6)

(i) In a similar experiment, another student used 0.040 mol of ethyl benzoate and obtained 5.12 g of benzoic acid.

Calculate the percentage yield of benzoic acid.

Suggest why the yield is not 100%.

Percentage yield _____ %

Suggestion _____

_____

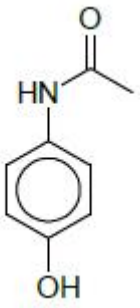
_____

(3)

(Total 18 marks)

Q4.

Paracetamol is a common analgesic used for the relief of pain. It has the structure shown.



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The melting point of paracetamol is 170 °C.
Paracetamol can be prepared from the reaction between 4-aminophenol ($HOC_6H_4NH_2$) and ethanoyl chloride.

(a) Write an equation for this reaction.

_____

(1)

(b) Name and outline the mechanism for this reaction. Use RNH_2 to represent 4–aminophenol.

Name of mechanism _____

Mechanism

(5)

(c) The paracetamol formed in this reaction is impure. It contains both soluble and insoluble impurities that must be removed by recrystallisation.

The properties of a suitable solvent for recrystallisation are shown.

- The paracetamol should dissolve when the solvent is hot but be almost insoluble when the solvent is cold.
- The impurities should either be insoluble in the solvent at all temperatures or soluble even in cold solvent.
- When a hot saturated solution of the paracetamol is cooled, as much product as possible should crystallise out, leaving soluble impurities in the solution.

A solvent has been suggested for this recrystallisation. It is a flammable liquid with a boiling point of 80 °C.

Outline how you would carry out an investigation to show that this solvent is suitable for the recrystallisation of the impure paracetamol. You should include brief practical details of how you would carry out your investigation.

You are **not** required to describe the full recrystallisation procedure.

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Explain how you would check that a recrystallisation process had been effective at producing a pure sample of paracetamol.

(6)

(d) When paracetamol is prepared by reacting an excess of 4-aminophenol with ethanoyl chloride, the expected percentage yield of impure paracetamol is 65%.

An expert practical chemist might expect to lose, at most, a further 20% of the impure product during recrystallisation.

A student started with 3.87 g of ethanoyl chloride.

After preparation of impure paracetamol followed by recrystallisation, the student actually obtained 4.07 g of pure paracetamol.

Calculate the mass of impure paracetamol expected from this experiment, based on a 65% yield.

Use your answer and the actual mass of pure paracetamol obtained, to comment on the statement that “the student has demonstrated expert practical skills”.

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_____

(4)

(e) Suggest why the student should **not** use this sample of paracetamol for the purposes of pain relief.

_____

_____

_____

(1)

(f) Suggest **two** reasons why, in an industrial situation, ethanoic anhydride would be preferred to ethanoyl chloride in the production of paracetamol.

1. _____

_____

2. _____

_____

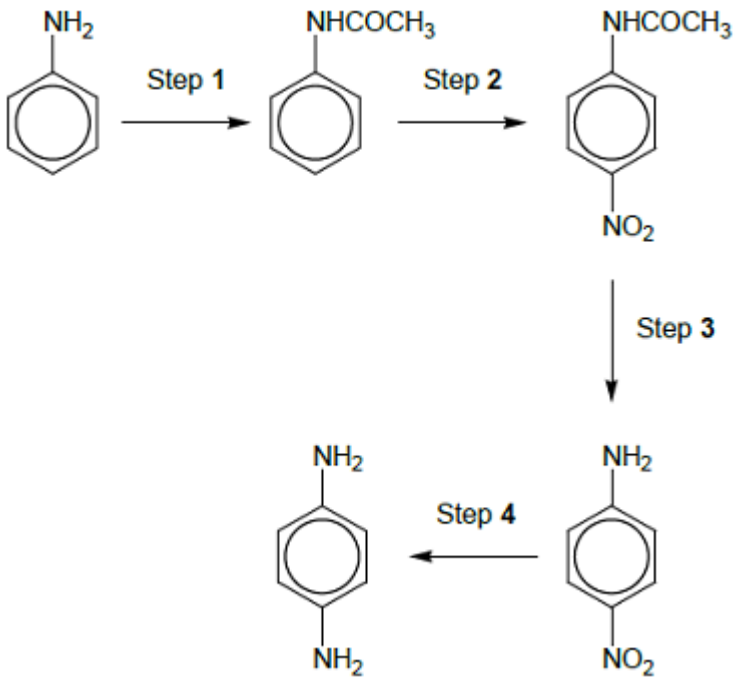
(2)

(Total 19 marks)

Q5.

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

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

Name of mechanism _____

Mechanism

(5)

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

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

Give reasons for each of the following practical steps.

The minimum quantity of hot water was used

_____

_____

_____

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

_____

_____

_____

The crystals were compressed in the funnel

_____

_____

_____

A little cold water was poured through the crystals

_____

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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.

_____

_____

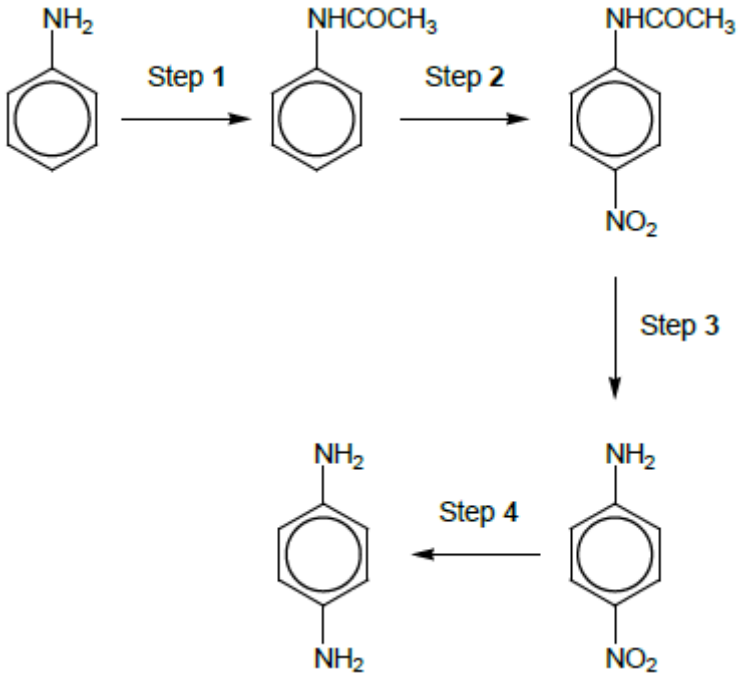
_____

_____

_____

(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.

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Percentage yield = _____%

(3)

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

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

_____

(1)

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

_____

(1)

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

_____

(1)

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

_____

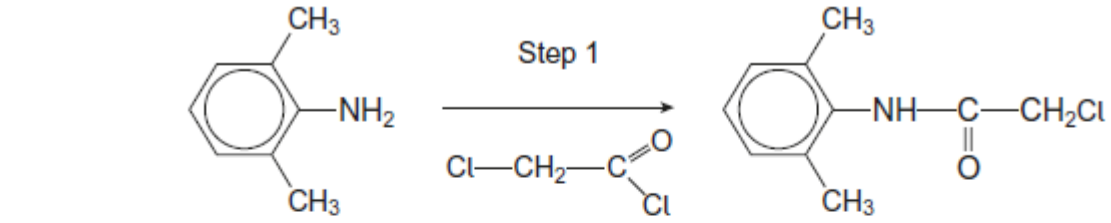
(1)

(Total 18 marks)

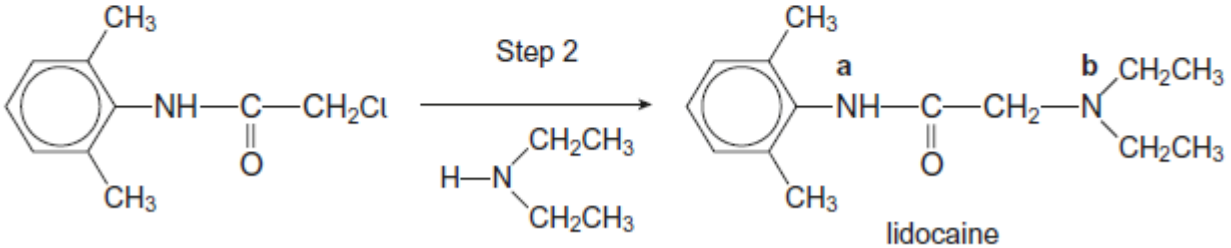
Q6.

Lidocaine is a local anaesthetic used in dentistry and in minor surgical operations.
The synthesis of lidocaine in 2 steps from 2,6-dimethylphenylamine is shown.

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X



Y lidocaine

(a) (i) Give the IUPAC name of reagent **X** in Step 1.

_____

(1)

(ii) Outline a mechanism for Step 1.
In your answer, use RNH_2 to represent 2,6-dimethylphenylamine.

(4)

(b) Name the mechanism for Step 2.

_____

(1)

(c) Which of these is the total number of peaks in the ^{13}C n.m.r spectrum of lidocaine?

Tick (✓) one box.

8 ☐ 9 ☐ 11 ☐ 12 ☐

(1)

(d) Calculate the percentage by mass of hydrogen in a molecule of lidocaine.

_____

_____

_____

(2)

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(e) Give the name, including the classification, of the functional group that contains the nitrogen atom labelled **b**.

_____

(1)

(f) Lidocaine is used medically as the salt lidocaine hydrochloride.

(i) Suggest which one of the nitrogen atoms labelled **a** or **b** is protonated in lidocaine hydrochloride. Explain your answer.

Nitrogen atom protonated _____

Explanation _____

_____

_____

_____

(3)

(ii) Suggest why lidocaine hydrochloride is used medically in preference to lidocaine.
Explain your answer.

_____

_____

_____

_____

(2)

(Total 15 marks)

Q7.

Esters are used as raw materials in the production of soaps and biodiesel.

(a) A student prepared an ester by two different methods.

Method **1** alcohol + acid anhydride

Method **2** alcohol + acyl chloride

(i) An ester was prepared using method **1**, by reacting $(CH_3)_2CHOH$ with $(CH_3CO)_2O$

Write an equation for this reaction and give the IUPAC name of the ester formed.

Equation

_____

IUPAC name of the ester _____

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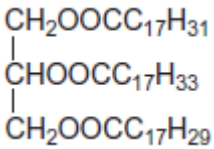
(2)

(ii) The same ester was prepared using method **2** by reacting $(CH_3)_2CHOH$ with CH_3COCl

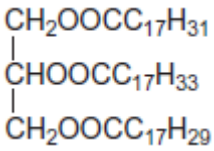
Outline a mechanism for this reaction.

(4)

(b) The ester shown occurs in vegetable oils.
It can be hydrolysed to make soap and can also be used to produce biodiesel.



(i) Write an equation for the reaction of this ester with sodium hydroxide to form soap.



(2)

(ii) Give the formula of the biodiesel molecule with the highest M_r that can be produced by reaction of this ester with methanol.

(1)

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(Total 9 marks)

Q8.

N-phenylethanamide is used as an inhibitor in hydrogen peroxide decomposition and also in the production of dyes.

N-phenylethanamide can be produced in a laboratory by the reaction between phenylammonium sulfate and an excess of ethanoic anhydride:

(a) A student carried out this preparation using 1.15 g of phenylammonium sulfate (M_r = 284.1) and excess ethanoic anhydride.

$$(C_6H_5NH_3)_2SO_4 + 2(CH_3CO)_2O \rightarrow 2C_6H_5NHCOCH_3 + 2CH_3COOH + H_2SO_4$$

(i) Calculate the maximum theoretical yield of N−phenylethanamide that could be produced in the reaction. Record your answer to an appropriate precision.

Show your working.

_____

_____

_____

_____

_____

_____

_____

(3)

(ii) In the preparation, the student produced 0.89 g of N−phenylethanamide.

Calculate the percentage yield for the reaction.

_____

_____

_____

_____

(1)

(b) The student purified the crude solid product, N−phenylethanamide, by recrystallisation.

(i) Outline the method that the student should use for this recrystallisation.

_____

_____

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_____

_____

_____

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_____

_____

_____

(4)

(ii) Outline how you would carry out a simple laboratory process to show that the recrystallised product is a pure sample of N−phenylethanamide.

_____

_____

_____

_____

_____

_____

_____

_____

(3)

(iii) Assume that the reaction goes to completion.

Suggest **two** practical reasons why the percentage yield for this reaction may **not** be 100%.

1. _____

_____

2. _____

_____

(2)

(c) The reaction to form N−phenylethanamide would happen much more quickly if the student used ethanoyl chloride instead of ethanoic anhydride.

Explain why the student might prefer to use ethanoic anhydride, even though it has a slower rate of reaction.

_____

_____

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(2)

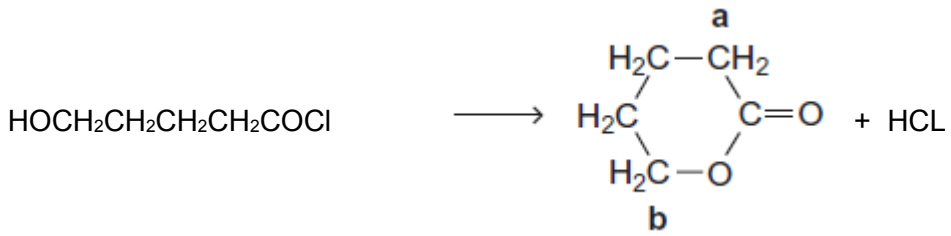
(Total 15 marks)

Q9.

This question is about some isomers of $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



H

(i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

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(7)

(ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in part (i).

Draw the repeating unit of the polyester and name the type of polymerisation involved.

_____

_____

_____

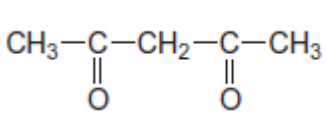
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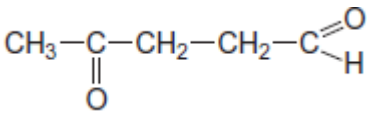
(2)

(b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.



J



K

_____

_____

_____

_____

_____

_____

_____

_____

(5)

(c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show

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stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^{1}H n.m.r. spectrum.

(5)
(Total 19 marks)

Q10.

(a) During the preparation of aspirin, it is necessary to filter the crude product under reduced pressure.

Draw a diagram to show the apparatus you would use to filter the crude product under reduced pressure. (Do **not** include the vacuum pump.)

(2)

(b) You are provided with a small sample of pure aspirin in a melting point tube. Describe briefly how you would determine an accurate value for the melting point of aspirin.

_____

_____

_____

_____

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(2)

(Total 4 marks)

Q11.

Aldehydes can be prepared from acyl chlorides.

State how an aldehyde could be tested to show whether it is contaminated with traces of unreacted acyl chloride.
State what you would observe.

Test _____

Observation _____

_____

(Total 2 marks)

Q12.

Acyl chlorides such as CH_3COCl are useful compounds in synthesis.

(a) The acyl chloride CH_3COCl reacts with benzene.

(i) Write an equation for this reaction and name the organic product.

Identify a catalyst for the reaction.

Write an equation to show how this catalyst reacts with CH_3COCl to produce a reactive intermediate.

_____

_____

_____

_____

_____

_____

_____

_____

(4)

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

Name of mechanism _____

Mechanism

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(4)

(b) Nucleophiles such as alcohols can react with CH_3COCl
The ion CH_3COO^- can act as a nucleophile in a similar way.

State the meaning of the term *nucleophile*.

Draw the structure of the organic product formed by the reaction of CH_3COO^- with CH_3COCl

Name the functional group produced in this reaction.

_____

_____

_____

_____

_____

_____

_____

_____

_____

(3)
(Total 11 marks)

Q13.

Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

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

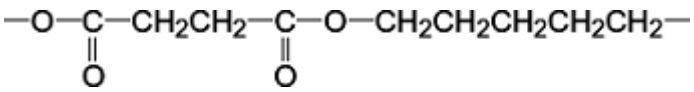
Mechanism

Name of organic product _____

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(5)

(b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



(i) Name the diol used.

_____

(1)

(ii) Draw the displayed formula of the diacyl chloride used.

(1)

(iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction _____

Explanation _____

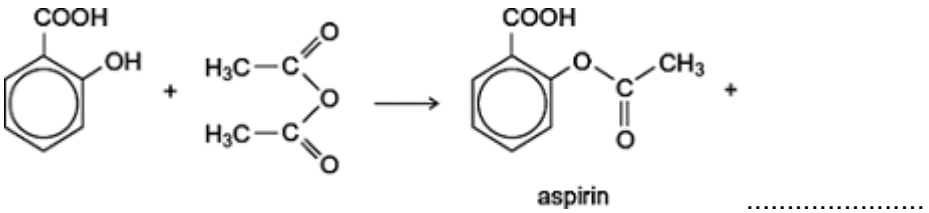
_____

_____

_____

(3)

(c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



(1)

(ii) Suggest a name for the mechanism for the reaction in part (c)(i).

_____

(1)

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(iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 _____

_____

_____

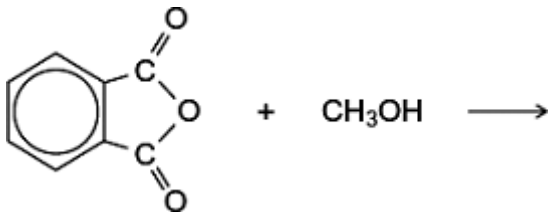
Advantage 2 _____

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_____

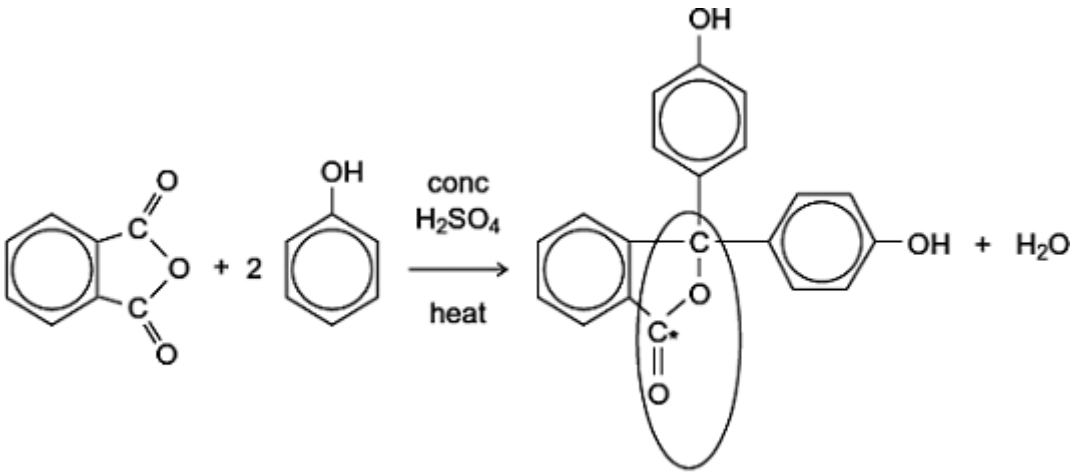
(2)

(d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product



(1)

(e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



(i) Name the functional group ringed in the structure of phenolphthalein.

_____

(1)

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

_____

(1)

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(iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

_____

(1)

(f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

(i) For **each** acid.alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	**Alkali**	**Tick box (✓)**
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2)

(ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

_____

(1)

(Total 21 marks)

Q14.

Salicylic acid can be used to make aspirin. Before using a sample of salicylic acid to make aspirin, a student purified the acid by recrystallisation. The method for recrystallisation is outlined below.

Step 1: The sample is dissolved in a minimum volume of hot water.
Step 2: The solution is filtered hot.
Step 3: The filtrate is cooled in ice to form crystals.
Step 4: The crystals are collected by filtration, washed with cold water and left to dry.

Explain the purpose of each underlined point.

Minimum volume _____

_____

Hot water_____

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_____

Filtered hot_____

_____

Cooled in ice _____

_____

Washed with cold water _____

_____

(Total 5 marks)

Q15.

The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of CH_3CH_2COCl and of $CH_3CH_2CH_2Cl$ with ammonia.

(a) For the reaction of CH_3CH_2COCl with ammonia, name and outline the mechanism and name the organic product.

_____

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_____

(6)

(b) For the reaction of $CH_3CH_2CH_2Cl$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

_____

_____

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(6)

(c) Suggest **one** reason why chlorobenzene (C_6H_5Cl) does **not** react with ammonia under normal conditions.

(1)

(Total 13 marks)

Q16.

Samples of 1-chloropropane and ethanoyl chloride can be distinguished by the addition of an aqueous solution of silver nitrate.
State what you would observe with each sample.

Observation with 1-chloropropane

Observation with ethanoyl chloride.

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(Total 2 marks)

Q17.

Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

(a) Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

(4)

(b) Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

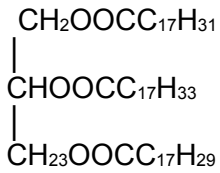
(3)

(c) Name and outline a mechanism for the reaction of CH_3COCl with CH_3OH to form an ester.

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(5)

(d) The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.



(3)

(e) Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradeable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

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(4)

(Total 19 marks)

Q18.

(a) Name and outline a mechanism for the reaction of $CH_3CH_2NH_2$ with CH_3CH_2COCl

Name the amide formed.

(6)

(b) Haloalkanes such as CH_3Cl are used in organic synthesis.

Outline a three-step synthesis of $CH_3CH_2NH_2$ starting from methane. Your first step should involve the formation of CH_3Cl

In your answer, identify the product of the second step and give the reagents and conditions for each step.

Equations and mechanisms are **not** required.

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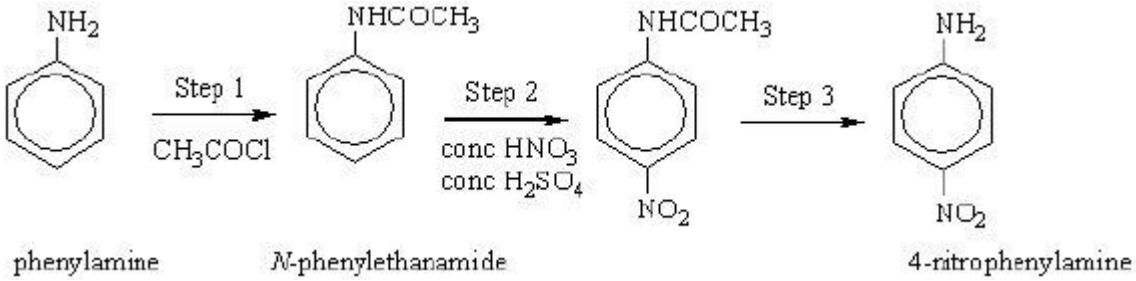
(6)

(Total 12 marks)

Q19.

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

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



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

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

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

_____

_____

_____

_____

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_____

(3)

(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.

_____

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(2)

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

(2)

(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.

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_____

_____

(4)

(Total 16 marks)

Q20.

(a) Write an equation for the formation of methyl propanoate, $CH_3CH_2COOCH_3$, from methanol and propanoic acid.

_____

(1)

(b) Name and outline a mechanism for the reaction between methanol and propanoyl chloride to form methyl propanoate.

Name of mechanism _____

Mechanism

(5)

(c) Propanoic anhydride could be used instead of propanoyl chloride in the preparation of methyl propanoate from methanol. Draw the structure of propanoic anhydride.

(1)

(d) (i) Give **one** advantage of the use of propanoyl chloride instead of propanoic acid in the laboratory preparation of methyl propanoate from methanol.

_____

_____

(ii) Give **one** advantage of the use of propanoic anhydride instead of propanoyl chloride in the industrial manufacture of methyl propanoate from methanol.

_____

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_____

(2)

(e) An ester contains a benzene ring. The mass spectrum of this ester shows a molecular ion peak at *m/z* = 136.

(i) Deduce the molecular formula of this ester.

_____

_____

_____

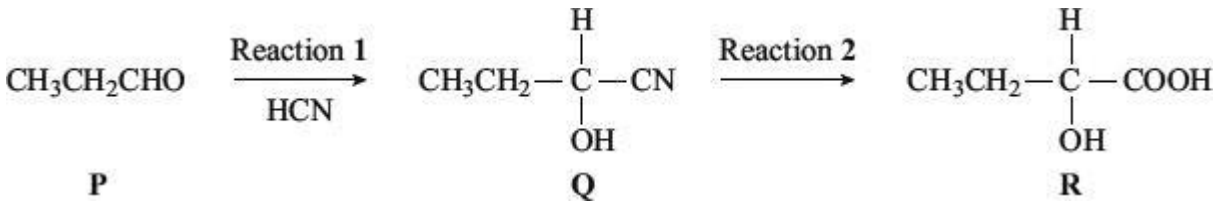
(ii) Draw **two** possible structures for this ester.

(3)

(Total 12 marks)

Q21.

Consider the sequence of reactions below.



(a) Name and outline a mechanism for Reaction **1**.

Name of mechanism _____

Mechanism

(5)

(b) (i) Name compound **Q**

_____

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(ii) The molecular formula of **Q** is C_4H_7NO. Draw the structure of the isomer of **Q** which shows geometrical isomerism and is formed by the reaction of ammonia with an acyl chloride.

(3)

(c) Draw the structure of the main organic product formed in each case when **R** reacts separately with the following substances:

(i) methanol in the presence of a few drops of concentrated sulphuric acid;

(ii) acidified potassium dichromate(VI);

(iii) concentrated sulphuric acid in an elimination reaction.

(3)
(Total 11 marks)

Q22.

(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

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(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)

Q23.

(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.

_____

_____

_____

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(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)

Q24.

(a) Addition reactions to both alkenes and carbonyl compounds can result in the

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formation of isomeric compounds.

(i) Choose an alkene with molecular formula C_4H_8 which reacts with HBr to form two structural isomers. Give the structures of these two isomers and name the type of structural isomerism shown.

Outline a mechanism for the formation of the major product.

(7)

(ii) Using HCN and a suitable carbonyl compound with molecular formula C_3H_6O, outline a mechanism for an addition reaction in which two isomers are produced.
Give the structures of the two isomers formed and state the type of isomerism shown.

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(7)

(b) Explain why ethanoyl chloride reacts readily with nucleophiles.
Write an equation for one nucleophilic addition–elimination reaction of ethanoyl chloride.
(A mechanism is not required.)

(4)

(Total 18 marks)

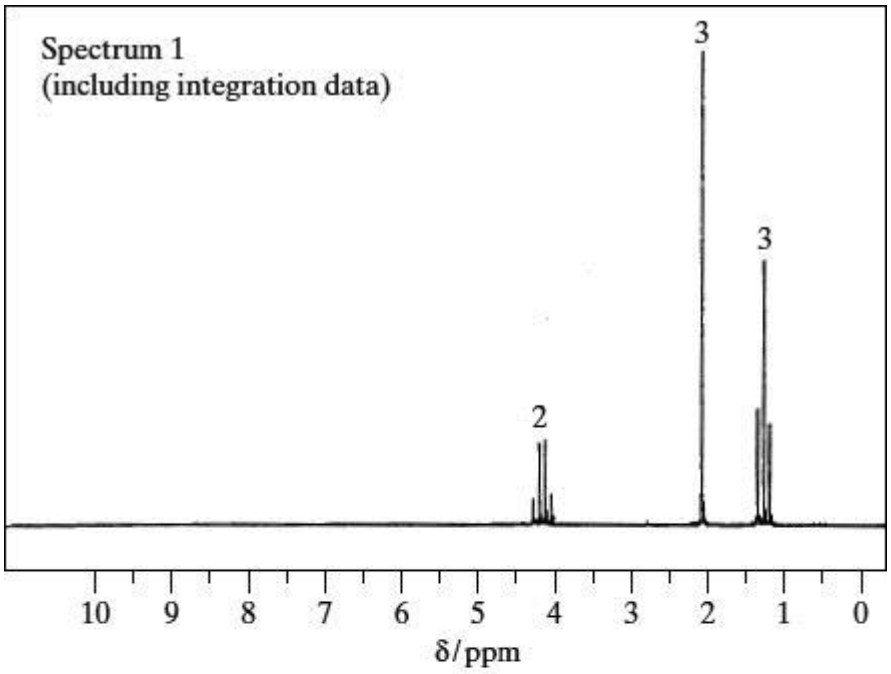
Q25.

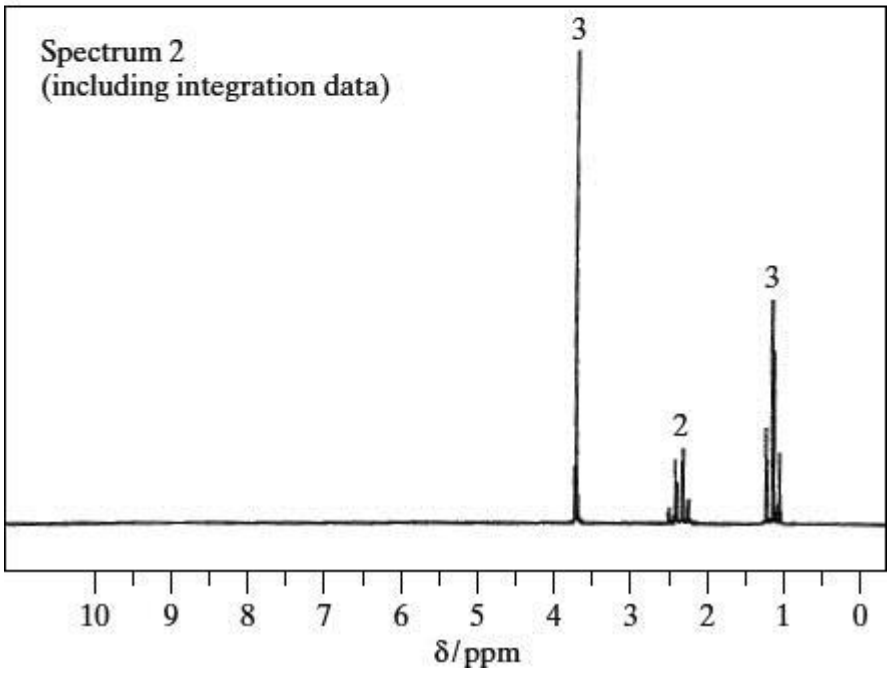
(a) Ester **X**, $CH_3CH_2COOCH_3$, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved.

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(6)

(b) The proton n.m.r. spectrum of **X** is shown below together with that of an isomeric ester, **Y**. Deduce which of Spectrum 1 and Spectrum 2 is that obtained from **X**. Use **Table 1** on the Data Sheet and the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.





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(4)

(Total 10 marks)

Q26.

(a) The gaseous reactants **W** and **X** were sealed in a flask and the mixture left until the following equilibrium had been established.

$2W(g) + X(g) \rightleftharpoons 3Y(g) + 2Z(g) \qquad \Delta H = -200 \text{ kJ mol}^{-1}$

Write an expression for the equilibrium constant, K_p, for this reaction.
State one change in the conditions which would both increase the rate of reaction and decrease the value of K_p. Explain your answers.

(7)

(b) Ethyl ethanoate can be prepared by the reactions shown below.

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Reaction 1

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ $\Delta H^{\ominus} = -2.0$ kJ mol^{-1}

Reaction 2

$CH_3COCl(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + HCl(g)$ $\Delta H^{\ominus} = -21.6$ kJ mol^{-1}

(i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 1** rather than by **Reaction 2**.

_____

_____

_____

_____

(2)

(ii) Use the information given above and the data below to calculate values for the standard entropy change, $\Delta S^{\ominus}$, and the standard free-energy change, $\Delta G^{\ominus}$, for **Reaction 2** at 298 K.

	$CH_3COCl(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$HCl(g)$
$S^{\ominus}$/JK^{1}mol^1	201	161	259	187

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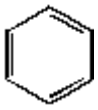
(6)

(Total 15 marks)

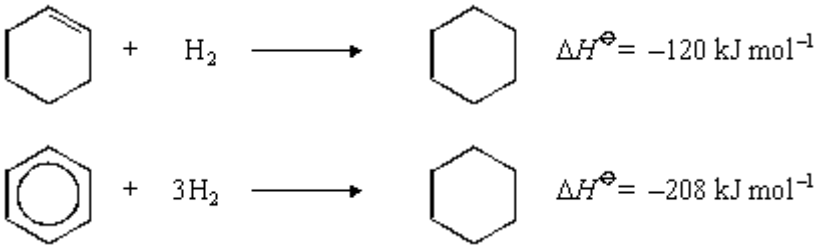
Q27.

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

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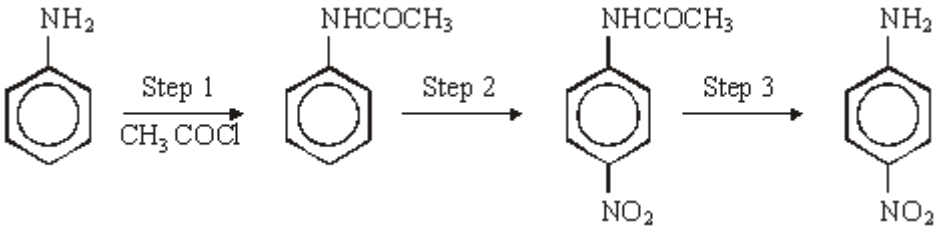


Give a reason for this difference in stability.



(4)

(b) Consider the following reaction sequence which starts from phenylamine.



(i) State and explain the difference in base strength between phenylamine and ammonia.

(3)

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(ii) Name and outline a mechanism for the reaction in Step 1 and name the organic product of Step 1.

(6)

(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.

(6)

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(iv) Name the type of linkage which is broken in Step 3 and suggest a suitable reagent for this reaction.

_____

_____

_____

_____

(2)

(Total 21 marks)

Q28.

(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.

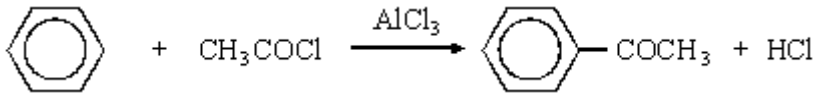
Mechanism

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.

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(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)

Q29.

(a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.110 mol of ethanol was maintained at 25 °C until the following equilibrium had been established.

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

The ethanoic acid present at equilibrium required 72.5 cm^3 of a 1.50 mol dm^{-3} solution of sodium hydroxide for complete reaction.

(i) Calculate the value of the equilibrium constant, K_c, for this reaction at 25 °C.

_____

_____

_____

_____

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_____

_____

_____

(7)

(ii) The enthalpy change for this reaction is quite small. By reference to the number and type of bonds broken and made, explain how this might have been predicted.

_____

_____

_____

_____

(2)

(b) Aspirin can be prepared by acylation using either ethanoyl chloride or ethanoic anhydride, as represented by the equations shown below.

$CH_3COCl + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + HCl$

$(CH_3CO)_2O + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + CH_3COOH$

(i) By a consideration of the intermolecular forces involved, explain why the product HCl is a gas but the product CH_3COOH is a liquid at room temperature.

_____

_____

_____

_____

(2)

(ii) Give **two** industrial advantages of using ethanoic anhydride rather than ethanoyl chloride in the manufacture of aspirin.

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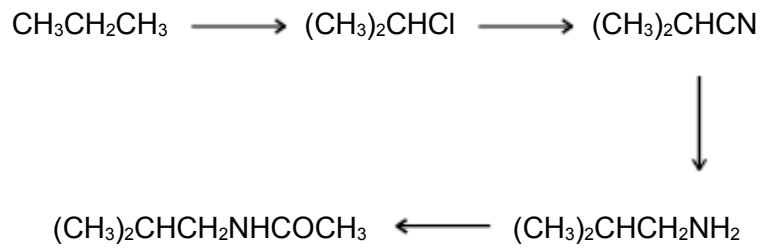
(2)

(Total 13 marks)

Q30.

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Which one of the following types of reaction mechanism is **not** involved in the above sequence?



A free-radical substitution

B nucleophilic substitution

C elimination

D nucleophilic addition-elimination

(Total 1 mark)

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