

AQA A-LEVEL CHEMISTRY • 7405

CHEMISTRY



EXAM QUESTION PACK

3.3.9 CARBOXYLIC ACIDS AND DERIVATIVES

SCORE

/379

PERCENTAGE

%

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Q1.

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

- (a) $\text{CH}_3\text{CH}_2\text{COCl}$ reacts with benzene in the presence of AlCl_3 in an electrophilic substitution reaction.

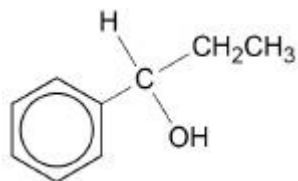
Give an equation for the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ with AlCl_3 to form the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

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 _____

(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)

- (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 $\text{CH}_3\text{CH}_2\text{COCl}$ and $\text{CH}_3\text{CH}_2\text{NH}_2$

Give the IUPAC name of the organic product.

Name of mechanism _____

Mechanism

IUPAC name of organic product _____

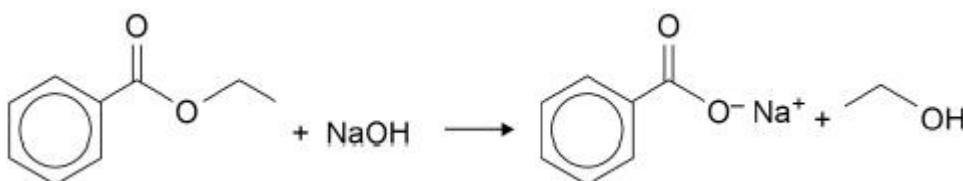
(6)

(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)

(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.

(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 _____ %

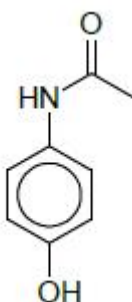
Suggestion _____

(3)

(Total 18 marks)

Q4.

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



The melting point of paracetamol is 170 °C.
Paracetamol can be prepared from the reaction between 4-aminophenol (HOC₆H₄NH₂) and ethanoyl chloride.

- (a) Write an equation for this reaction.

(1)

- (b) Name and outline the mechanism for this reaction. Use RNH₂ 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.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

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

A student started with 3.87 g of ethanoyl chloride.

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

[illegible]

(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. _____

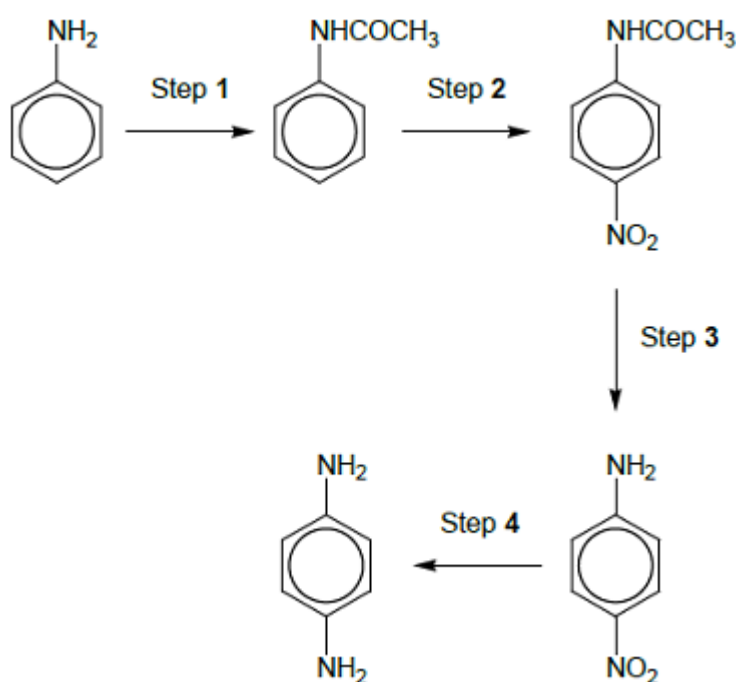
(2)

(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

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

Name of mechanism _____

Mechanism

(5)

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

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

After a few minutes, the crystals were removed from the funnel and weighed. A small sample was then used to find the melting point.

Give reasons for each of the following practical steps.

The minimum quantity of hot water was used

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

The crystals were compressed in the funnel

A little cold water was poured through the crystals

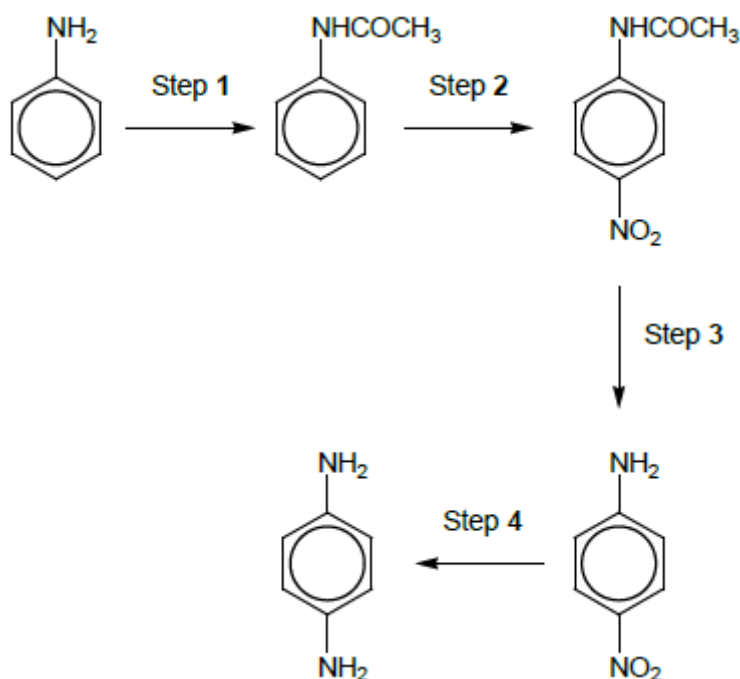
(4)

- (c) The melting point of the sample in part (b) was found to be slightly lower than a data-book value.

Suggest the most likely impurity to have caused this low value and an improvement to the method so that a more accurate value for the melting point would be obtained.

(2)

The figure above is repeated here to help you answer the following questions.



- (d) In an experiment starting with 5.05 g of phenylamine, 4.82 g of purified product were obtained in step 1.

Calculate the percentage yield in this reaction.
Give your answer to the appropriate number of significant figures.

Percentage yield = _____ %

(3)

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

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

(1)

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

(1)

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

(1)

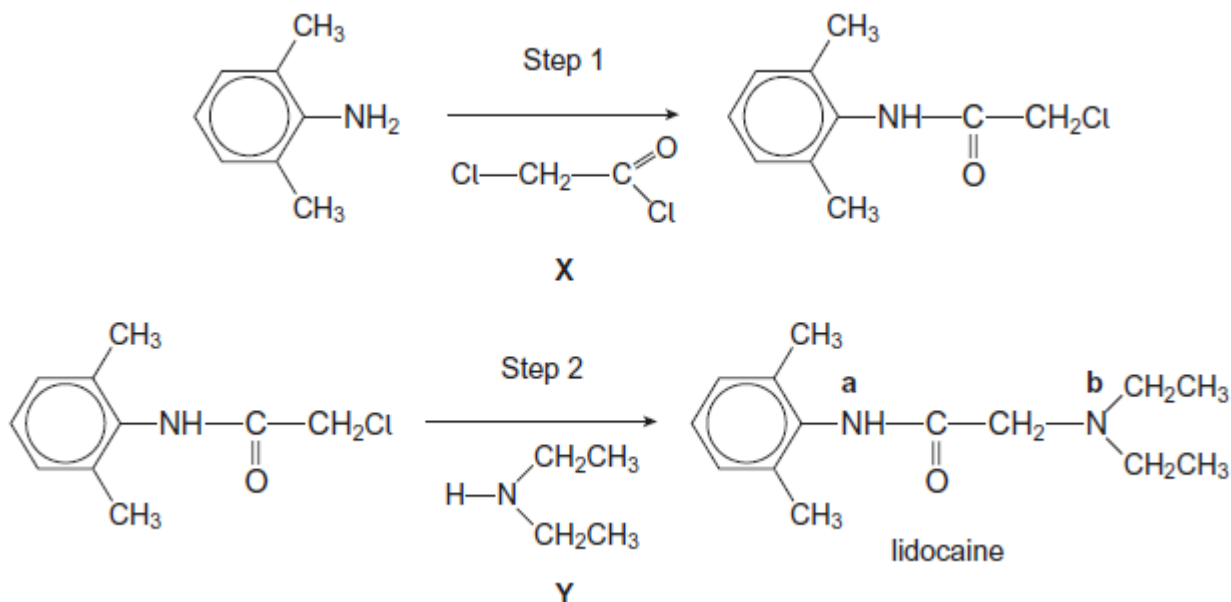
- (h) Identify the reagents used in step 4.

(1)

(Total 18 marks)

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.



- (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)

- (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 $(\text{CH}_3)_2\text{CHOH}$ with $(\text{CH}_3\text{CO})_2\text{O}$

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

Equation

IUPAC name of the ester _____

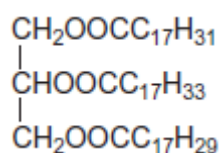
(2)

- (ii) The same ester was prepared using method **2** by reacting $(\text{CH}_3)_2\text{CHOH}$ with CH_3COCl

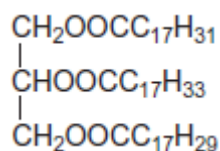
Outline a mechanism for this reaction.

(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.

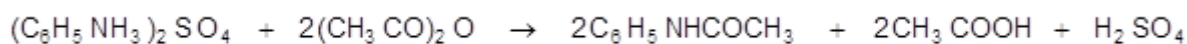
(1)

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.



- (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.

(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.

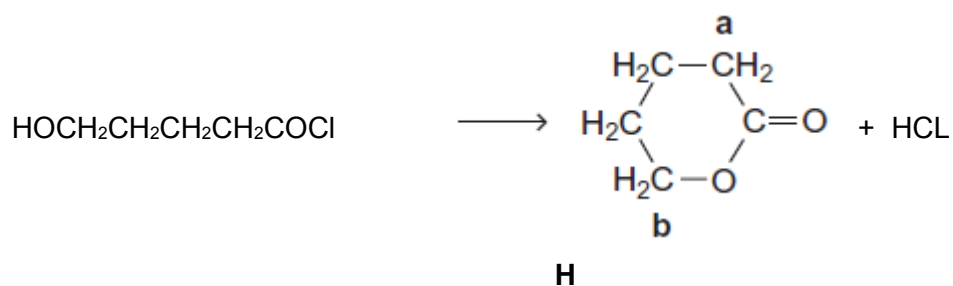
Explain why the student might prefer to use ethanoic anhydride, even though it has a slower rate of reaction.

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.



- (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**.

(7)

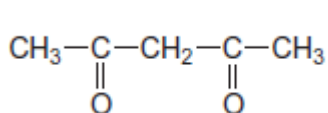
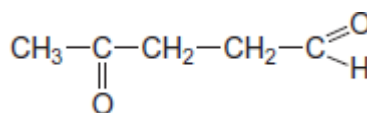
- (ii) $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$ can also react to form a polyester in a mechanism similar to that in part (i).

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

(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 $\text{C}_5\text{H}_8\text{O}_2$.
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

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 ^1H 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.

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

(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.

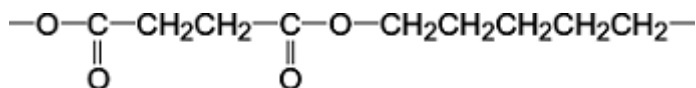
- (a) Outline a mechanism for the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ with CH_3OH and name the organic product formed.

Mechanism

Name of organic product _____

(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.

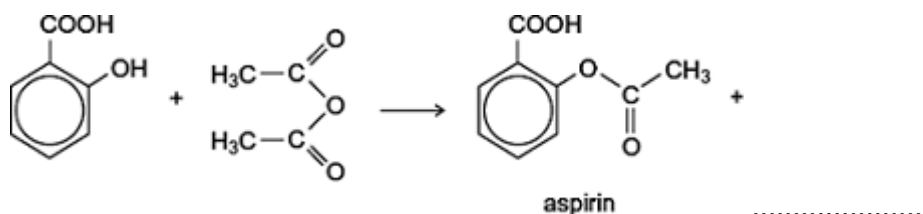
Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

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)

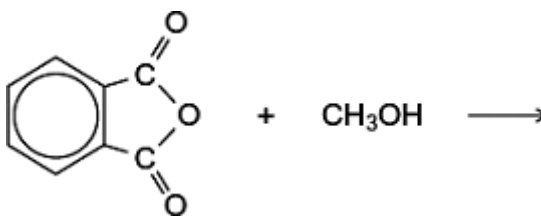
- (iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 _____

Advantage 2 _____

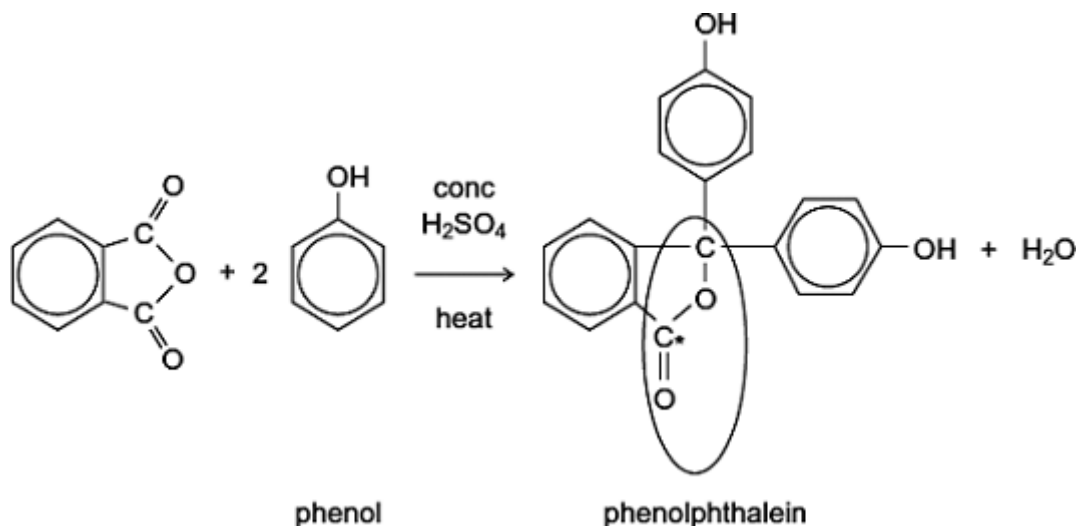
(2)

- (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)

- (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 _____

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 $\text{CH}_3\text{CH}_2\text{COCl}$ and of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ with ammonia.

- (a) For the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ with ammonia, name and outline the mechanism and name the organic product.

[illegible]

(6)

- (b) For the reaction of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

(6)

- (1)

Q16.

State what you would observe with each sample.

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.

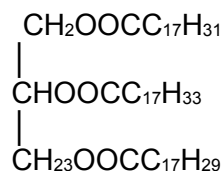
Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

(3)

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

(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 biodegradable, it is preferable to recycle objects made from Terylene.

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

Q18.

- (a) Name and outline a mechanism for the reaction of $\text{CH}_3\text{CH}_2\text{NH}_2$ with $\text{CH}_3\text{CH}_2\text{COCl}$

Name the amide formed.

(6)

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

Outline a three-step synthesis of $\text{CH}_3\text{CH}_2\text{NH}_2$ 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.

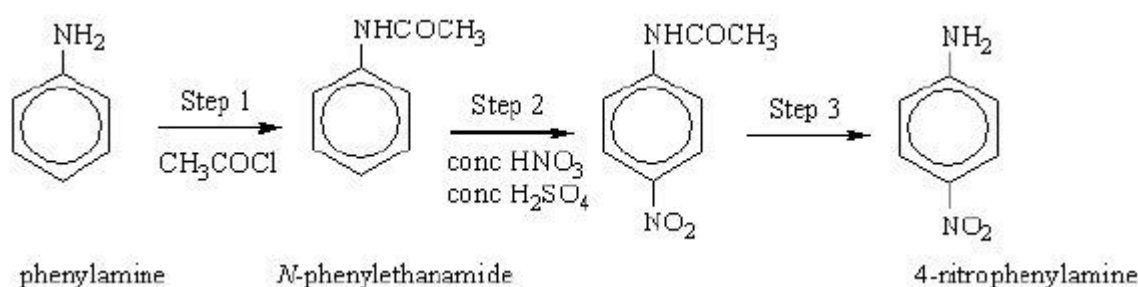
Equations and mechanisms are **not** required.

(6)
(Total 12 marks)

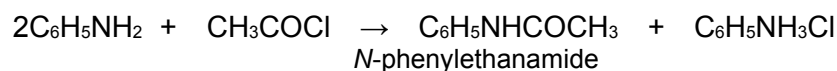
Q19.

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.



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

(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.

(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.

(4)
(Total 16 marks)

Q20.

- (a) Write an equation for the formation of methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$, 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.

(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.

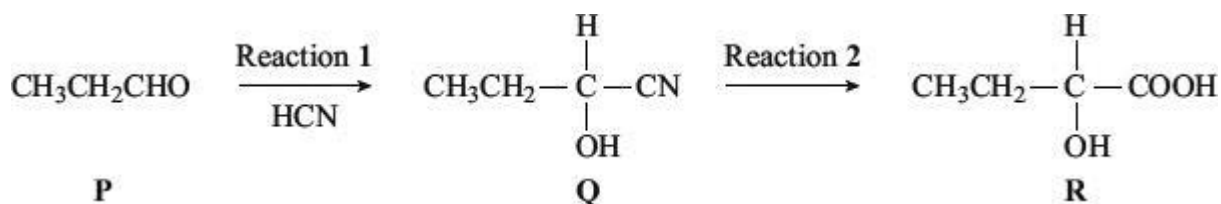
(ii) Draw **two** possible structures for this ester.

(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**

- (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

(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, $\text{CH}_3\text{CH}_2\text{COCl}$, and methylamine, CH_3NH_2 . Draw the structure of the organic product.

(6)

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

(5)

- (c) Write an equation for the reaction of propanoyl chloride with water. An excess of water is added to 1.48 g of propanoyl chloride. Aqueous sodium hydroxide is then added from a burette to the resulting solution. Calculate the volume of 0.42 mol dm^{-3} aqueous sodium hydroxide needed to react exactly with the mixture formed.

(5)

(Total 16 marks)

Q24.

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

(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.

[illegible]

(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.

[illegible]

(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)

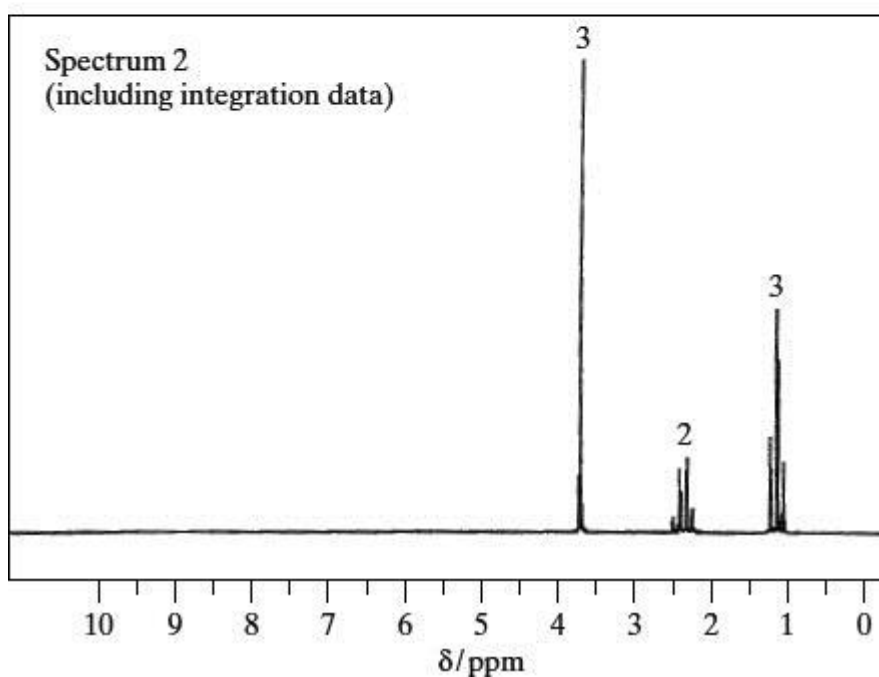
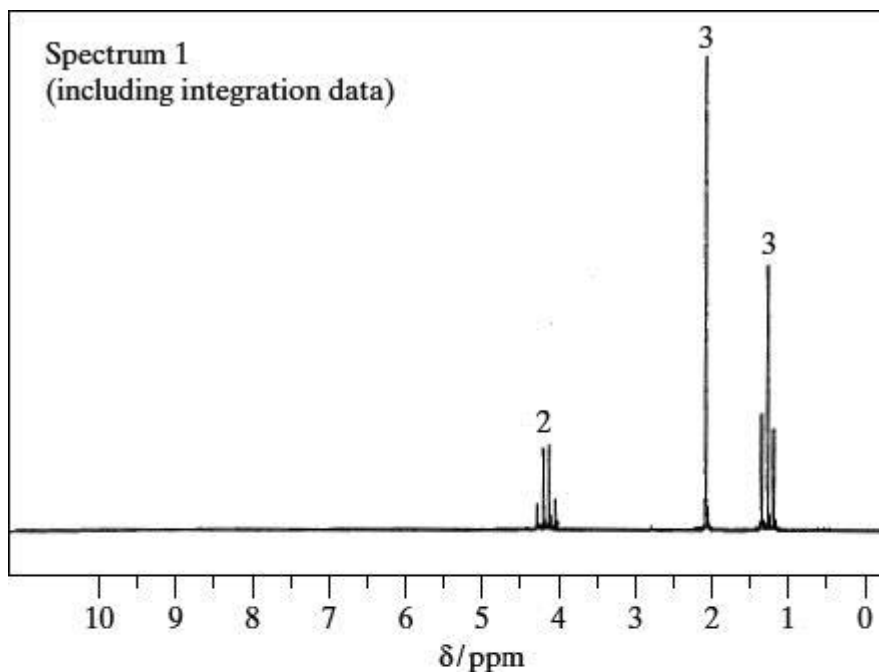
(Total 18 marks)

Q25.

- (a) Ester **X**, $\text{CH}_3\text{CH}_2\text{COOCH}_3$, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved.

(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**.

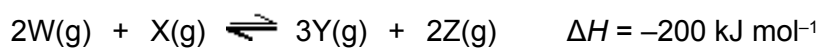


(4)

(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.



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.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

(7)

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

$$\text{CH}_3\text{COOH(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{H}_2\text{O(l)} \quad \Delta H^\ominus = -2.0 \text{ kJ mol}^{-1}$$
$$\text{CH}_3\text{COCl(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{HCl(g)} \quad \Delta H^\ominus = -21.6 \text{ kJ mol}^{-1}$$

- (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 ₃ COCl(l)	C ₂ H ₅ OH(l)	CH ₃ COOC ₂ H ₅ (l)	HCl(g)
S [⊖] /JK ⁻¹ mol ⁻¹	201	161	259	187

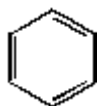
[illegible]

(6)

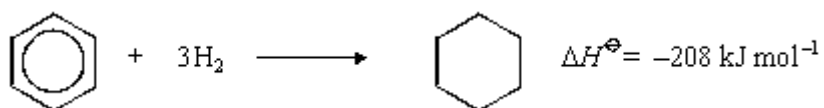
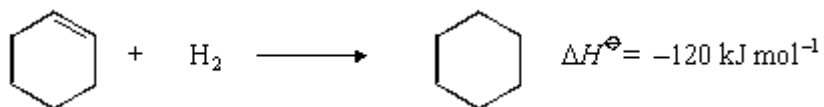
(Total 15 marks)

Q27.

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

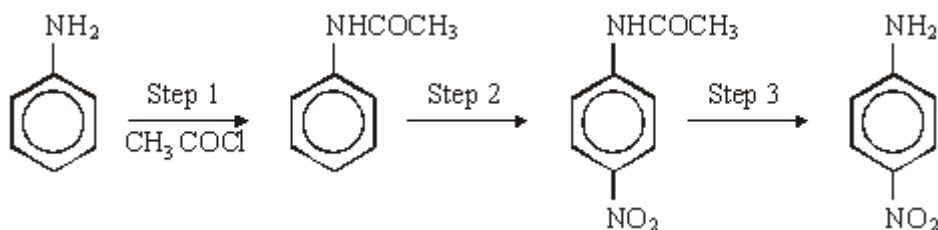


Give a reason for this difference in stability.



(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)

- [illegible]

(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.

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STEMUP.CO.UK

- (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 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ with HCN and name the product.

Mechanism

Name of product _____

(5)

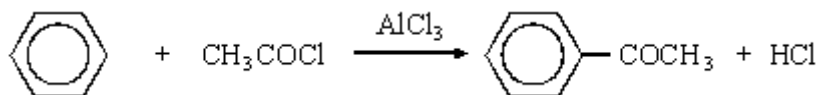
- (b) Outline a mechanism for the reaction of CH_3OH with $\text{CH}_3\text{CH}_2\text{COCl}$ and name the organic product.

Mechanism

Name of organic product _____

(5)

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



- (i) Give the formula of the reactive intermediate.

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

(4)

(Total 14 marks)

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.



The ethanoic acid present at equilibrium required 72.5 cm³ of a 1.50 mol dm⁻³ solution of sodium hydroxide for complete reaction.

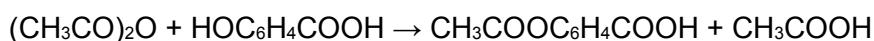
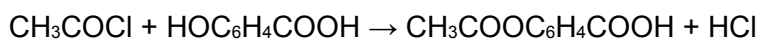
- (i) Calculate the value of the equilibrium constant, K_c , for this reaction at 25 °C.

(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.



- (i) By a consideration of the intermolecular forces involved, explain why the product HCl is a gas but the product CH₃COOH is a liquid at room temperature.

(2)

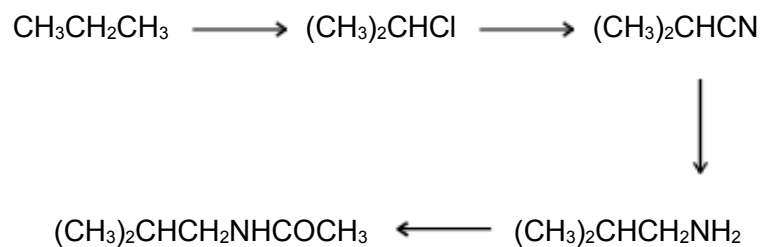
- (ii) Give **two** industrial advantages of using ethanoic anhydride rather than ethanoyl chloride in the manufacture of aspirin.

(2)

(Total 13 marks)

Q30.

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)

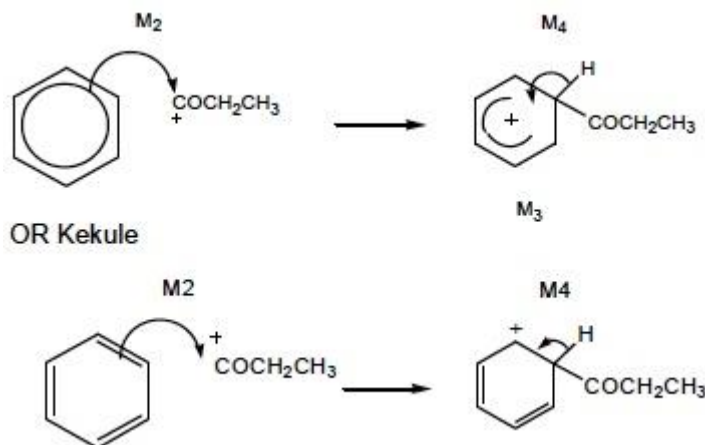
Mark schemes

Q1.



Allow + on C or O in equation –
But must be on C in mechanism

M1



M2 Arrow from inside hexagon to C or + on C

1

M3 Structure of intermediate

- horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller
- + in intermediate not too close to C1 (allow on or “below” a line from C2 to C6)

1

M4 Arrow from bond into hexagon (Unless Kekule)

- Can allow M4 arrow independent of wrong M3 structure
- + on H in intermediate loses M3 not M4
- Ignore Cl⁻ and AlCl₄⁻
- used in M4

1

(b) Either...

1-phenylpropan-1-ol

1

NaBH₄ / LiAlH₄

1

Nucleophilic addition

1

Or...

1-phenylpropan-1-ol

1

H₂ with Ni/Pd/Pt

Addition/hydrogenation

1

Both numbers needed for names

1

Ignore solvents

(c) Misty fumes / steamy fumes

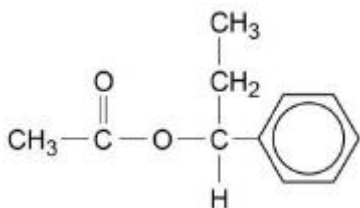
Allow sweet/fruity smell / white fumes

Not smoke

1

(Nucleophilic) addition-elimination

1

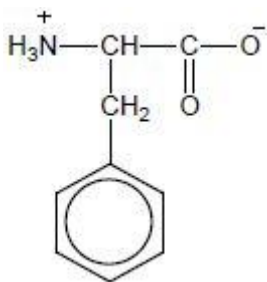


1

[10]

Q2.

(a)

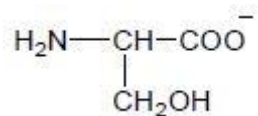


Allow -CO₂⁻

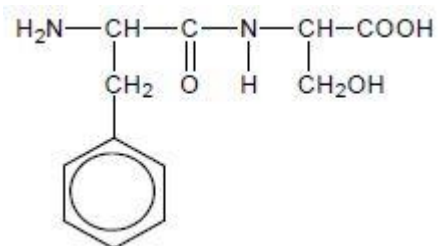
Allow ⁺H₃N- and NH₃⁺-

1

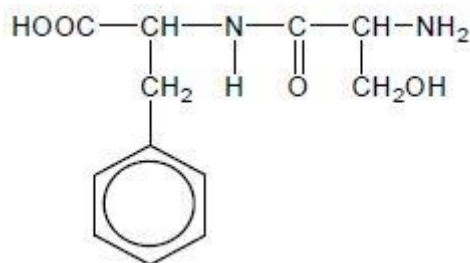
(b)



(c)



1



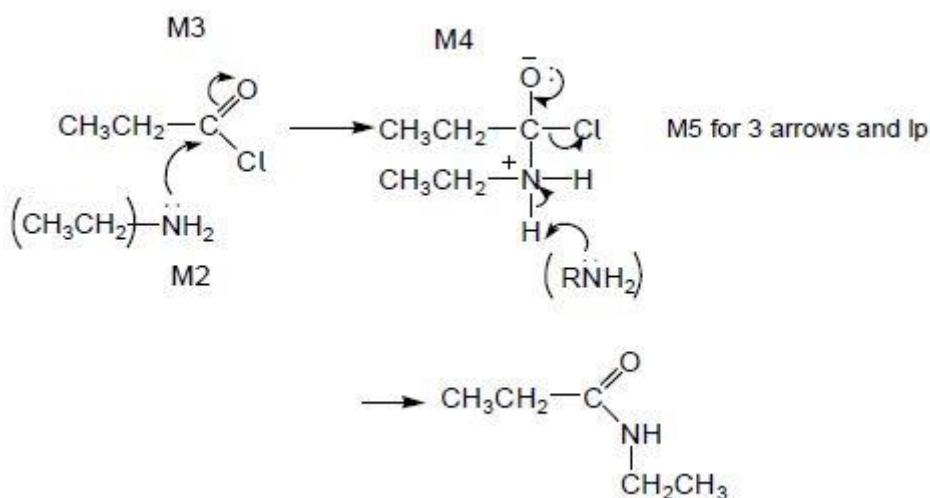
1

If same wrong amino acid twice – max 1

(d) (nucleophilic) addition-elimination

Not electrophilic addition-elimination.

M1



M2 for arrow from lp on N to C

(or to space half way between N and C)

Ignore δ^+ and δ^- unless wrong

M3 for arrow from C=O bond to O

Not score M3 as an independent first step, but can allow M2 for attack on C⁺ produced

If Cl lost at this stage, Max 1 for mechanism for M2

M4 for structure of ion including 2 charges

(+ on N must be correct in both cases if drawn twice)

M5 for 3 arrows and lp on O

- may be scored in two steps

Ignore use of RNH₂ to remove H⁺ in M5, but penalise use of Cl⁻

M2-5

N-ethylpropanamide

M6

[10]

Q3.

- (a) allows smaller bubbles to form / prevents the formation of (very) large bubbles
ALLOW provides large surface area for bubbles to form on
IGNORE 'air'
NOT no bubbles form / prevents bubbles forming

1

- (b) (Mass of ester = $1.05 \times 5.0 = 5.25\text{g}$)
amount of ester = $5.25 / 150.0 = 0.0350\text{ mol}$

1

amount of NaOH = $30 \times 2 / 1000 = 0.06\text{ mol}$

1

OR

(Mass of ester = $1.05 \times 5.0 = 5.25\text{g}$)
amount of ester = $5.25 / 150.0 = 0.0350\text{ mol}$

1

Vol of 0.035 mol of NaOH = $(0.035/2) \times 1000 = 17.5\text{ cm}^3$
(so 30 cm³ used is an excess)

1

OR

amount of NaOH = $30 \times 2 / 1000 = 0.06\text{ mol}$

1

0.06 mol of ester = 9 g = 8.57 cm³
(only 5 cm³ used so NaOH in excess)

1

Mark independently

Max 2

- (c) To ensure that the ester is completely hydrolysed / to ensure all the ester reacts

ALLOW to ensure the other reagent has completely reacted

1

- (d) Many organic compounds / the ester / ethanol are flammable

ALLOW prevent ignition of any flammable vapours formed

1

- (e) Reflux allows reactant vapours (of volatile organic compounds) to be returned to the reaction mixture / does not allow any reactant vapour to escape

IGNORE reference to products

1

- (f) $\text{C}_6\text{H}_5\text{COONa} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{NaCl}$

Allow ionic equation.

ALLOW molecular formulae ($\text{C}_7\text{H}_5\text{O}_2\text{Na}$ and $\text{C}_7\text{H}_6\text{O}_2$)

ALLOW skeletal benzene ring

1

- (g) Sodium benzoate soluble because it is ionic

IGNORE polar

1

Benzoic acid insoluble because: despite the polarity of the COOH group / ability of COOH to form H-bonds, the benzene ring is non-polar.

ALLOW 'part of molecule' or 'one end' for COOH

1

- (h) Dissolve crude product in hot solvent/water

ALLOW ethanol

If no M1 max = 4

1

of minimum volume

ALLOW reference to saturated soln as alternative to 'min vol'

1

Filter (hot to remove insoluble impurities)

IGNORE use of Buchner funnel here

1

Cool to recrystallise

apply list principle for each additional process in an incorrect method but IGNORE additional m.pt determination

1

Filter under reduced pressure / with Buchner/Hirsch apparatus

1

wash (with cold solvent) **and** dry

1

- (i) $5.12 / 122 (= 0.042 \text{ mol})$

method mark

1

$$(0.042/0.04) \times 100 = 105 \%$$

ecf for M1/0.04

or calculation that 0.04 mol of benzoic = 4.88 g (M1) so

$$\% \text{ yield} = (5.12/4.88) \times 100 = 105\%$$

1

Product not dried / impurities present in product

Only allow M3 if M2>100%

1

[18]

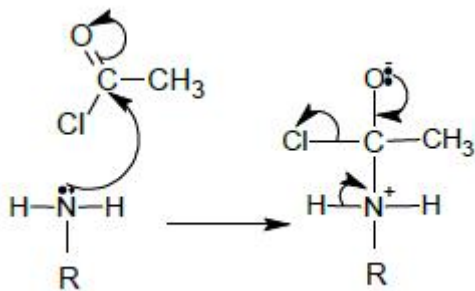
Q4.

- (a) $2\text{HO}-\text{C}_6\text{H}_4-\text{NH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{HO}-\text{C}_6\text{H}_4-\text{NHCOCH}_3 + \text{HO}-\text{C}_6\text{H}_4-\text{NH}_3^+\text{Cl}^-$
 $\text{HO}-\text{C}_6\text{H}_4-\text{NH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{HO}-\text{C}_6\text{H}_4-\text{NHCOCH}_3 + \text{HCl}$

1

- (b) (Nucleophilic) Addition-elimination.

1



M2 = Arrow from lone pair on N to carbon in C=O.

1

M3 = Arrow from the bond in CO to the O.

1

M3 = Correct intermediate with + on N and - on O.

1

M4 = Three arrows and lone pair.

1

- (c) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

Level 3

Outlines a workable process with clear decision-making process. Gives a method for melting point determination with detailed reference to the melting point of 170 ± 2 °C.

5-6 marks

Level 2

Outlines a workable process with some indication of decision-making. Gives a method for melting point determination without detailed reference to the melting point of 170 ± 2 °C.

3-4 marks

Level 1

Partially outlines a potentially workable process. Suggests need for melting point determination.

1-2 marks

Level 0

Insufficient correct chemistry to warrant a mark.

0 marks

Indicative Chemistry content

- Place a small amount of pure paracetamol in a test-tube.
- Add small volume ($0.5\text{--}1.0\text{ cm}^3$) of possible solvent
- Shake/stir.
- If paracetamol dissolves then solvent unsuitable.
- Heat (with suitable awareness of flammability and boiling point; e.g. hot – not boiling – water bath).
- If paracetamol does not dissolve = unsuitable.
- If paracetamol dissolves partially try adding more

solvent.

- *If/when completely dissolved place test-tube in ice-water bath.*
- *If crystals form = suitable.*
- *Effectiveness determined by measuring melting point.*
- *Purity indicated by melting point being sharp and close to 170 °C.*

6

- (d) Amount of ethanoyl chloride = $3.87 / 78.5 = 0.0493$ mol

1

(Theoretical mass of paracetamol = $0.0493 \times 151 = 7.44$ g)

Mass expected = $(65/100) \times 7.44 = 4.84$ g

1

Loss in mass on recrystallisation = $4.84 - 4.07 = 0.77$

1

Percentage loss in mass = $(0.77 / 4.84) \times 100 = 15.9 \%$

This suggests that the student has demonstrated expert practical skills as less than 20 % loss during recrystallisation.

Allow comment that it is unlikely student would be better than expert chemist so final product may not be dry thus increasing apparent mass obtained.

1

- (e) There may still be small amounts of impurities.

1

- (f) Any **two** from:

- less exothermic reaction
- easier to control
- dangerous gas not evolved
- ethanoic anhydride is a cheaper or more easily recycled reagent.

2

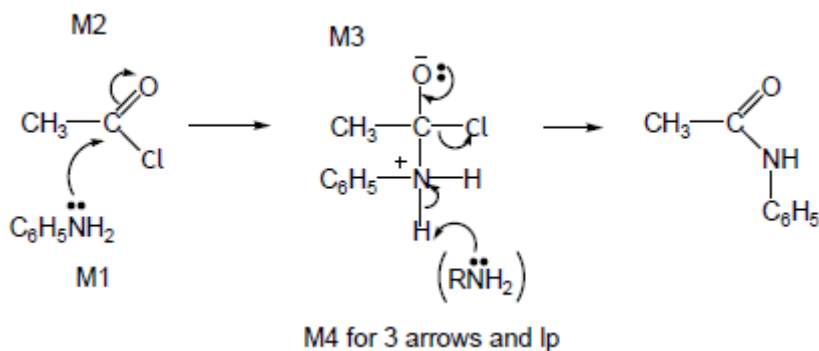
[19]

Q5.

- (a) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

1



Allow C₆H₅ or benzene ring

Allow attack by :NH₂C₆H₅

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

M3 for correct structure with charges but lone pair on O is part of M4

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

4

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

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

1

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

Yield lower if warm / solubility higher if warm

1

The crystals were compressed in the funnel:

Air passes through the sample not just round it

Allow better drying but not water squeezed out

1

A little cold water was poured through the crystals:

To wash away soluble impurities

1

(c) **Water**

Do not allow unreacted reagents

1

Press the sample of crystals between filter papers

Allow give the sample time to dry in air

1

(d) ***M_r* product = 135.0**

1

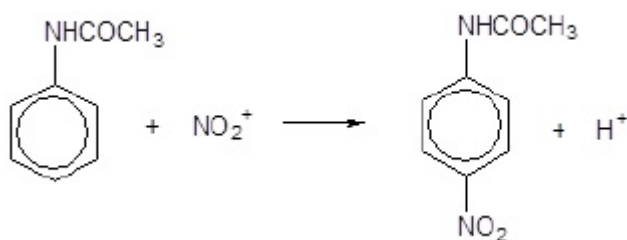
$$\text{Expected mass} = 5.05 \times \frac{135.0}{93.0} = 7.33 \text{ g}$$

1

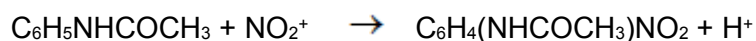
$$\text{Percentage yield} = \frac{4.82}{7.33} \times 100 = 65.75 = 65.8(\%)$$

Answer must be given to this precision

(e)



OR



1

(f) Electrophilic substitution

1

(g) Hydrolysis

1

(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

Q6.

(a) (i) (2-)chloroethan (-1-) oyl chloride

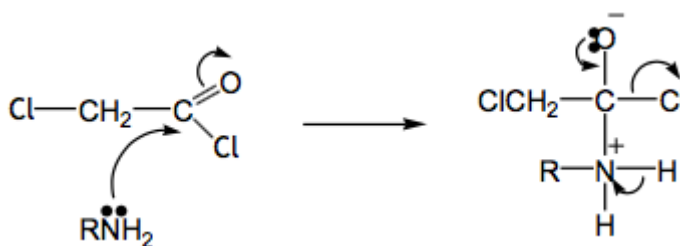
2 not required but penalise 1- or other numbers at start.

Ignore 1 in ethanoyl

Ignore hyphens, commas, spaces

1

(ii)



M1 for arrow from lp on N to C

(or to space half way between N and C)

If full amine drawn, ignore slips except in -NH₂

M2 for arrow from C=O bond to O

Not score M2 as an independent first step, but can allow M1 for attack on C⁺ produced

If Cl lost at this stage, Max 1 for M1

M3 for structure of ion including 2 charges

M4 for 3 arrows and lp on O

- may be scored in two steps

Ignore use of RNH_2 to remove H^+ in M4, but penalise use of Cl^-

4

- (b) Nucleophilic substitution

Allow minor spelling errors e.g. nucleophyllic

1

- (c) 9

1

- (d) $M_r = 234(.0)$

9.4 scores 2 marks

1

% H = 9.4(0)

$$M2 = \frac{22}{M1} \times 100$$

If $M_r = 234$ not shown, can score M1 if their answer $\times 234 =$ their no of H

1

- (e) Tertiary amine OR 3° amine OR III° amine

Ignore N- substituted

1

- (f) (i) If **a** given: CE=0, can only score if answer given is **b**

M1 lp on N^b or on **b**

M2 alkyl groups donate electron density or positive inductive effect or electron donating groups attached

M3 (lp on N^b) more available or protonated amine stabilised or better lp donor/ H^+ acceptor

Ignore reference to nucleophiles

NOTE – there is NO mark for **b** alone

Alternatives

M1 lp on N^a or on **a**

M2 lp or electrons (on N^a) delocalised into ring /towards O in $\text{C}=\text{O}$

M3 (lp on N^a) less available (to bond to H^+ /accept proton)

1

1

1

- (ii) Salt is ionic

Independent marks

1

(More) soluble (in blood/body fluids/water)

1

Q7.



Allow $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)_2$ and $\text{CH}_3\text{CO}_2\text{H}$

Ignore $(\text{CH}_3)_2-\text{C}$ in equation

1

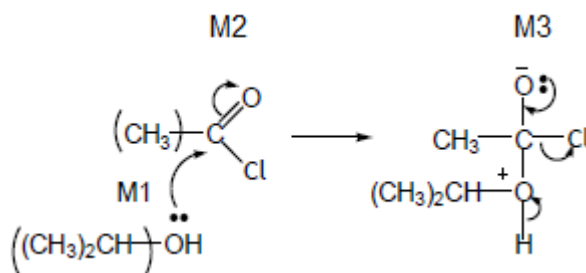
(1)-methylethyl ethanoate OR

Propan-2-yl ethanoate

Ignore extra or missing spaces, commas or hyphens

1

(ii)



M4 for 3 arrows and lp

NO Mark for name of mechanism

M1 for lone pair on O and arrow to C or to mid-point of space between O and C

M2 for arrow from C=O bond to O

- M2 not allowed independent of M1, but allow M1 for correct attack on C+
- + rather than $\delta+$ on C=O loses M2
- If Cl lost with C=O breaking, max1 for M1

M3 for correct structure with charges (penalise wrong alcohol here) but lone pair on O is part of M4

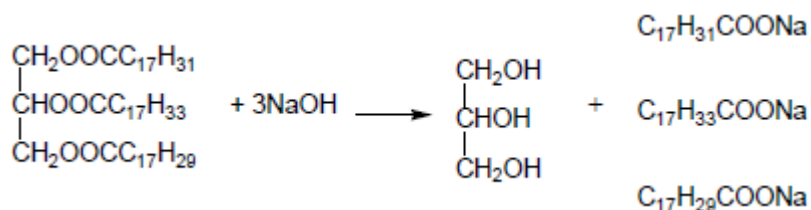
Penalise $(\text{CH}_3)_2-\text{C}$ in M3

M4 for lone pair on O and three arrows

- Only allow M4 after correct / very close M3
- M4 can be gained over more than one structure
- Ignore Cl- removing H^+

4

(b) (i)



- (ii) $C_{17}H_{33}COOCH_3$
Allow $C_{19}H_{36}O_2$

1

[9]

Q8.

- (a) (i) M_r N-phenylethanamide = 135.0

1

Theoretical yield = $135.0 \times 2 (1.15 / 284.1) = 1.09 \text{ g}$

1

Answer recorded to 3 significant figures.

1

- (ii) $\frac{0.89}{\text{Ans to (a)}} \times 100$

= 81.4 %

Mark consequentially to (a)

Allow 81 to 82

1

- (b) (i) Dissolve the product in the **minimum** volume of water / solvent (in a boiling tube / beaker)

If dissolving is not mentioned, CE = 0 / 4

1

Hot water / solvent

Steps must be in a logical order to score all 4 marks

1

Allow the solution to cool and allow crystals to form.

1

Filter off the pure product under reduced pressure / using a Buchner funnel and side arm flask

Ignore source of vacuum for filtration (electric pump, water pump, etc.)

1

- (ii) Measure the melting point

1

Use of melting point apparatus or oil bath

1

Sharp melting point / melting point matches data source value

1

- (iii) Any **two** from:
Product left in the beaker or glassware
Sample was still wet
Sample lost during recrystallisation.

Do not allow "sample lost" without clarification.

2 Max

- (c) An identified hazard of ethanoyl chloride

E.g. "Violent reaction", "harmful", "reacts violently with water"

Do not allow "toxic", "irritant" (unless linked with HCl gas).

1

HCl gas / fumes released / HCl not released when ethanoic anhydride used

1

[15]

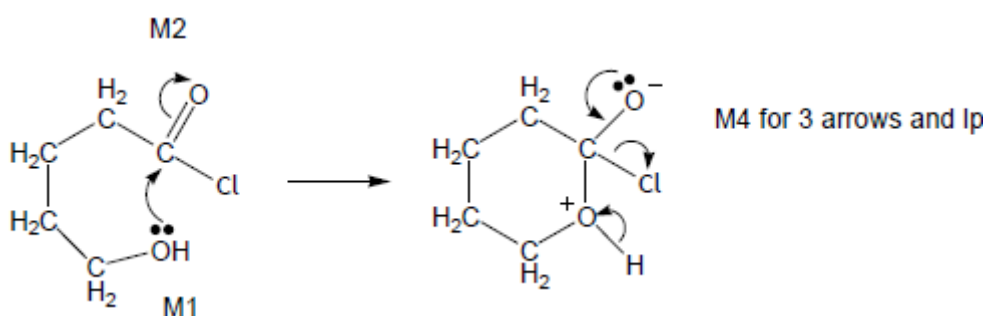
Q9.

- (a) (i) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

Ignore esterification

1



M3 for structure

- If wrong nucleophile used or O-H broken in first step, can only score M2.
- M2 not allowed independent of M1, but allow M1 for correct attack on C⁺
- + rather than δ^+ on C=O loses M2.
- If Cl lost with C=O breaking lose M2.
- M3 for correct structure with charges but lone pair on O is part of M4.
- Only allow M4 after correct / very close M3.
- Ignore HCl shown as a product.

4

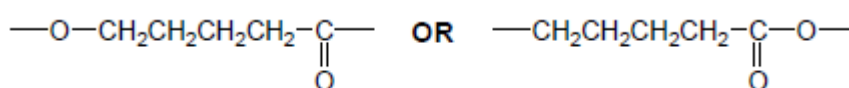
- a 20-50 (ppm) or single value or range entirely within this range
If values not specified as a or b then assume first is a.

1

- b 50-90 (ppm) or single value or range entirely within this range

1

- (ii)

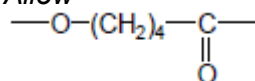


Must have trailing bonds, but ignore n.

1

OR $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}-$ OR $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-$

Allow



but not $-\text{C}_4\text{H}_8-$

one unit only

Condensation

1

(b)

	Tollens'	Fehling's / Benedicts	Acidified potassium dichromate
--	----------	-----------------------	--------------------------------

Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on.

1

J	No reaction / no (visible) change / no silver mirror	No reaction / no (visible) change / stays blue / no red ppt	No reaction / no (visible) change / stays orange / does not turn green
----------	---	--	---

Ignore 'clear', 'nothing'.

Penalise wrong starting colour for dichromate.

1

K	Silver <u>mirror</u> / grey <u>ppt</u>	Red <u>ppt</u> (allow brick red or red-orange)	(orange) turns green
----------	---	---	----------------------

1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

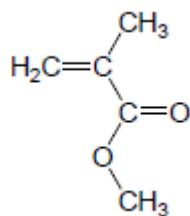
Ignore details of splitting.

If values not specified as J or K then assume first is J.

1

- (c) If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.

L
ester



OR $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$

All $\text{C}_5\text{H}_8\text{O}_2$ L to P must have $\text{C}=\text{C}$.

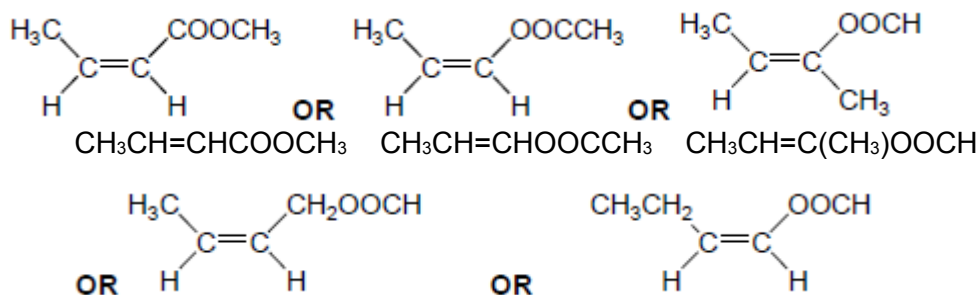
Allow CH_3- .

Allow $-\text{CO}_2\text{CH}_3$ etc.

Allow $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$.

1

M
ester



$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OOCH}$

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHOOCH}$

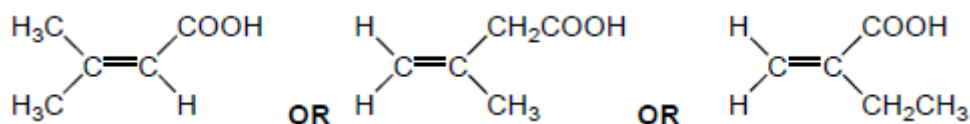
Allow either E-Z isomer.

Allow CH_3- or C_2H_5- but not CH_2CH_3- .

Allow $\text{CH}_3\text{CHCHCOOCH}_3$ etc.

1

N
acid



$(\text{CH}_3)_2\text{C}=\text{CHCOOH}$

$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{COOH}$

$\text{H}_2\text{C}=\text{C}(\text{COOH})\text{CH}_2$

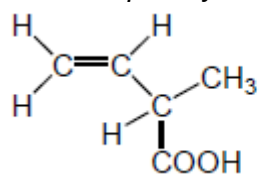
CH_3

Allow CH_3- or C_2H_5- but not CH_2CH_3- .

Allow $-\text{CO}_2\text{H}$.

Not cyclic isomers.

Not the optically active isomer.



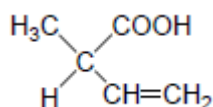
which is P anyway

Allow $(\text{CH}_3)_2\text{CCHCOOH}$ etc.

1

P

acid



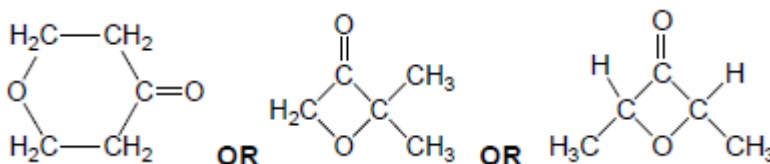
Allow $-\text{CO}_2\text{H}$.



Allow $\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{CHCH}_2$ or
 $\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{C}_2\text{H}_3$.

1

Q



Not cyclic esters.

1

[19]

Q10.

- (a) Side-arm flask / side-arm test tube

Do not allow sealed side-arm flask.

1

Flat-bottomed filter funnel with filter paper clearly shown

Either Buchner or Hirsch versions are suitable.

Allow Hirsch funnel and horizontal filter paper.

Allow three-dimensional filter funnels.

Do not allow standard Y-shaped funnel.

Do not allow sealed funnel.

If it is not clearly air-tight between the funnel and the flask,
maximum 1 mark.

1

- (b) Heat melting point tube in an oil bath

Accept 'melting point apparatus' or Thiele tube.

Do not accept water bath.

1

slowly near the melting point

Ignore any additional correct details.

Apply list principle for additional incorrect details.

1

[4]

Q11.

Test

silver nitrate (solution) (M1)

Allow an alternative soluble silver salt eg fluoride, sulfate.

Do not allow 'silver ions' but can access second mark.

Incorrect formula loses this mark but can access second mark.

Do not allow 'silver' or an insoluble silver salt and **cannot** access second mark.

Ignore references to acidification of the silver nitrate.

If an acid is specified it should be nitric acid, but allow sulfuric acid in this case as there are no metal ions present.

If hydrochloric acid is used, CE = 0 / 2.

Do not allow 'add water'.

1

Observation

white precipitate (**M2**)

Ignore 'cloudy'.

Do not allow 'white fumes' or 'effervescence'.

Do not allow this mark if test reagent is incorrect or missing.

Allow named indicator paper or named indicator solution for **M1**.

Allow correct colour change for **M2**.

1

[2]

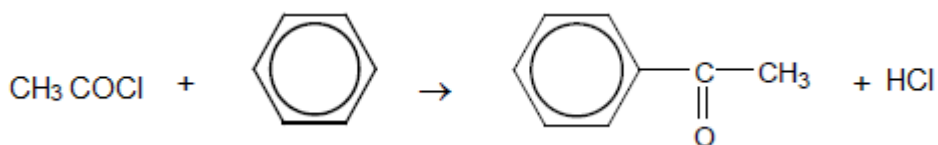
Q12.



Not molecular formulae Not allow $\text{C}_6\text{H}_5\text{CH}_3\text{CO}$

1

OR



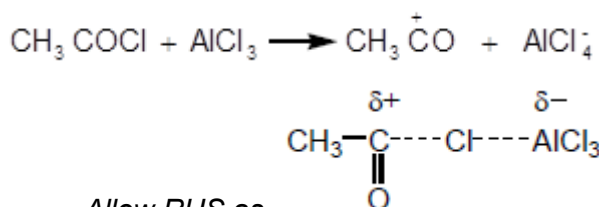
phenylethanone

Ignore number 1 in name but penalise other numbers

1

AlCl_3 can be scored in equation

1



Allow RHS as

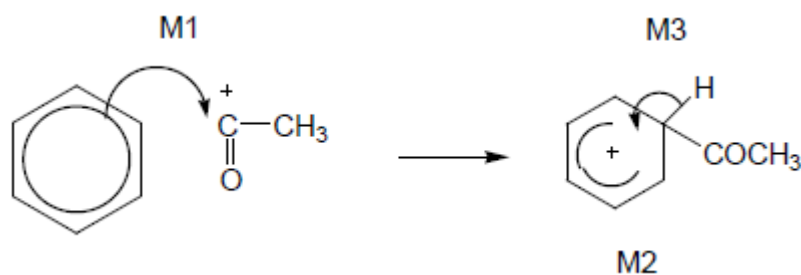
Allow + on C or O in equation but + must be on C in mechanism below

Ignore curly arrows in balanced equation even if wrong

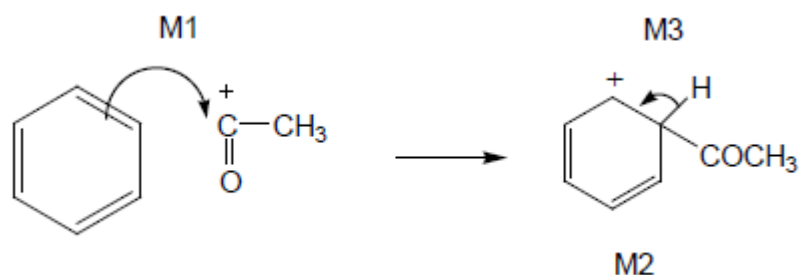
1

(ii) Electrophilic substitution

1



OR

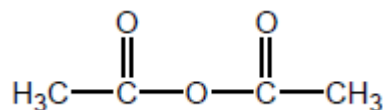


- M1 arrow from within hexagon to C or to + on C
- + must be on C of CH_3CO in mechanism
- + in intermediate not too close to C1
- Gap in horseshoe must be centred approximately around C1
- M3 arrow into hexagon unless Kekulé
- Allow M3 arrow independent of M2 structure,
- ie + on H in intermediate loses M2 not M3
- Ignore base removing H for M3

3

(b) Electron pair donor or lone pair donor*Allow donator**Allow lone pair used in description of (dative) bond formation*

1

*Allow $(\text{CH}_3\text{CO})_2\text{O}$*

1

(acid) anhydride

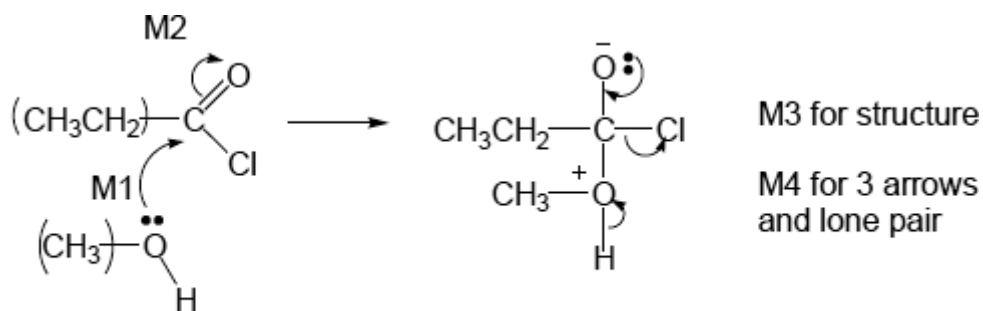
Allow ethanoic anhydride but not any other anhydride

1

[11]

Q13.

(a)



methyl propanoate

(NO mark for name of mechanism)

- M2 not allowed independent of M1, but allow M1 for correct attack on C⁺
- + rather than δ⁺ on C=O loses M2
- If Cl lost with C=O breaking, max1 for M1
- M3 for correct structure with charges but lp on O is part of M4
- only allow M4 after correct/very close M3
- ignore Cl⁻ removing H⁺

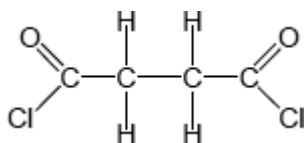
4

(b) (i) pentane-1,5-diol

Second 'e' and numbers needed

Allow 1,5-pentanediol but this is not IUPAC name

(ii)



Must show ALL bonds

1

(iii) All three marks are independent

M1 (base or alkaline) Hydrolysis (allow close spelling)

1

Allow (nucleophilic) addition-elimination or saponification

M2 δ⁺ C in polyester

1

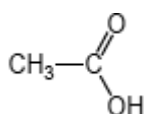
M3 reacts with OH⁻ or hydroxide ion

1

Not reacts with NaOH

1

(c) (i)



Allow CH₃COOH or CH₃CO₂H

1

(ii) (nucleophilic) addition-elimination

Both addition and elimination needed and in that order

OR

(nucleophilic) addition followed by elimination

*Do **not** allow electrophilic addition-elimination / esterification*

Ignore acylation

1

(iii) any **two** from: ethanoic anhydride is

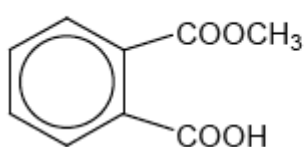
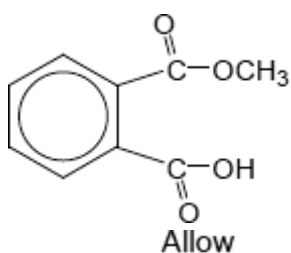
- less corrosive
- less vulnerable to hydrolysis
- less dangerous to use,
- less violent/exothermic/vigorous reaction OR more controllable rxn
- does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl
- less volatile

NOT COST

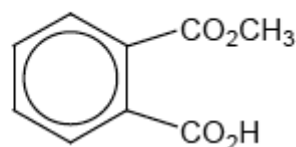
List principle beyond two answers

2

(d)



or



1

(e) (i) ester

*Do **not** allow ether*

Ignore functional group/linkage/bond

1

(ii) 12 or twelve (peaks)

1

(iii) 160 – 185

Allow a number or range within these limits

Penalize extra ranges given

Ignore units

1

(f) (i)

sulfuric acid	sodium hydroxide	✓
hydrochloric acid	ammonia	X or blank
ethanoic acid	potassium hydroxide	✓
nitric acid	methylamine	X or blank

4 correct scores 2

3 correct scores 1

2 or 1 correct scores 0

2

(ii) Pink to colourless

Allow 'red' OR 'purple' OR 'magenta' instead of 'pink'

*Do **not** allow 'clear' instead of 'colourless'*

1

[21]

Q14.

Minimum volume and hot water:

Note that this question is worth a total of 5 marks.

Any **two** from:

to obtain saturated solution

to increase yield / reduce amount left in solution

enable crystallisation (on cooling)

Do not allow 'because acid doesn't dissolve well in cold water'.

Max 2

Filtered hot: to remove insoluble impurities / to prevent crystals forming during filtration

1

Cooled in ice: to increase amount of crystals that are formed

Do not allow 'to cool quickly'.

1

Washed with cold water: to remove soluble impurities

Allow 'washing with hot water would dissolve some of the crystals'.

1

[5]

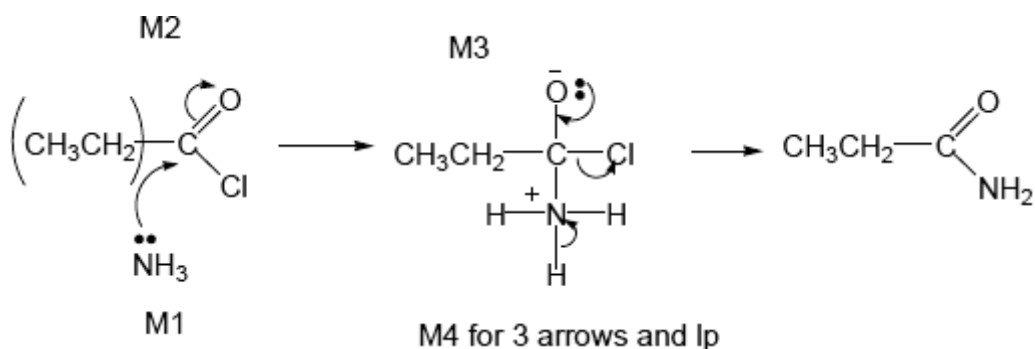
Q15.

(a) (Nucleophilic) addition-elimination

- *Minus sign on NH_3 loses M1 (but not M4 also)*

- M2 not allowed independent of M1, but

1



- allow M1 for correct attack on C+
- + rather than $\delta+$ on C=O loses M2
- **If Cl lost with C=O breaking, max1 for M1**
- **M3** for correct structure with charges but lp on O is part of **M4**
- only allow **M4** after correct/very close **M3**
- For **M4**, ignore NH_3 removing H^+ but lose **M4** for Cl^- removing H^+ in mechanism,
- but ignore HCl shown as a product

4

propanamide (Ignore -1-)

penalise other numbers

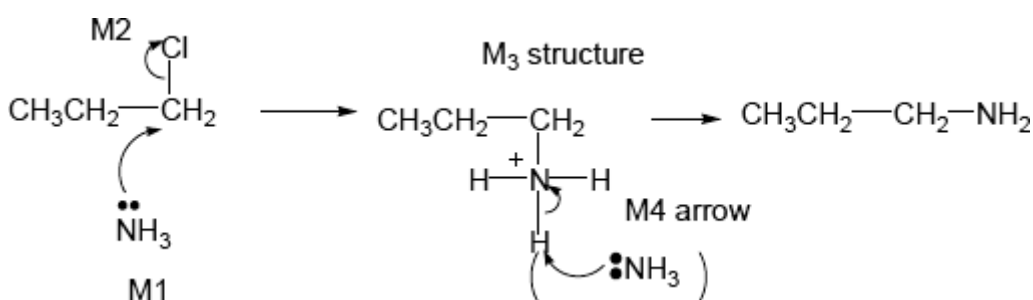
penalise propaneamide and N-propanamide

1

(b) Nucleophilic substitution

- Minus sign on NH_3 loses M1 (not M4 also)
- + rather than $\delta+$ on C=O loses M2

1



- ALLOW $\text{SN}1$ so allow M2 for loss of Cl^- before attack of NH_3 on C^+ for M1
- only allow M4 after correct/very close M3
- For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism,

Propylamine (ignore number 1)

- but ignore HCl shown as a product

4

or propan-1-amine or 1-aminopropane (number 1 needed)

penalise other numbers

allow 1-propanamine

1

(c) electron rich ring or benzene or pi cloud repels nucleophile/ammonia

Allow

- *C–Cl bond is short/stronger than in haloalkane*
- *C–Cl is less polar than in haloalkane*
- *resonance stabilisation between ring and Cl*

1

[13]

Q16.

1-chloropropane no visible change

Accept 'small amount of precipitate' or 'precipitate forms slowly'.

1

ethanoyl chloride white precipitate

Accept 'large amount of precipitate' or 'precipitate forms immediately'.

1

[2]

Q17.

(a) **M1** $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

not $\text{C}_3\text{H}_7\text{COOH}$

1

M2 $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{C}_2\text{H}_5\text{OH}$

1

M3 $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$

allow $\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$

penalise M3 for wrong products and unbalanced equation

1

M4 H_2SO_4 or HCl or H_3PO_4 conc or dil or neither

not HNO_3

1

(b) **M1** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

1

not $\text{C}_4\text{H}_9\text{OH}$

M2 $(\text{CH}_3\text{CO})_2\text{O}$

1

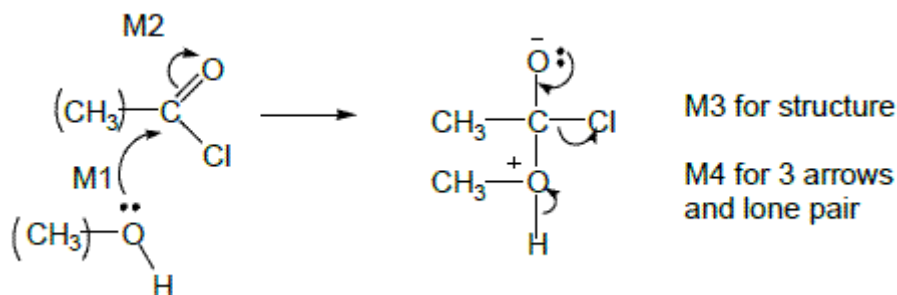
M3 $\rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{COOH}$

allow $\text{CH}_3\text{COOC}_4\text{H}_9$

penalise M3 for wrong products and unbalanced equation

1

(c) (nucleophilic) addition-elimination



not acylation alone

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

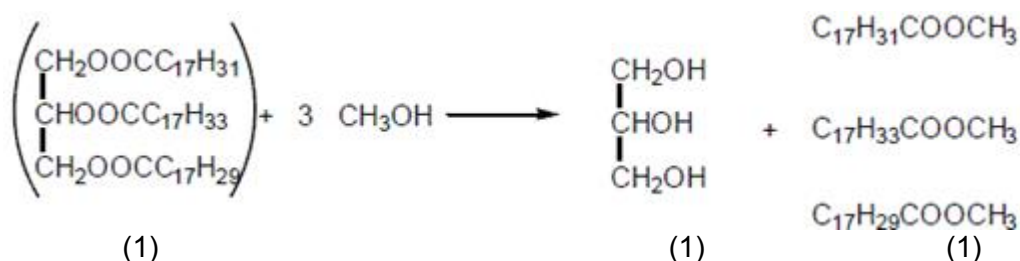
+C=O loses M2

only allow M4 after correct or v close M3

ignore Cl⁻ removing H⁺

5

(d)



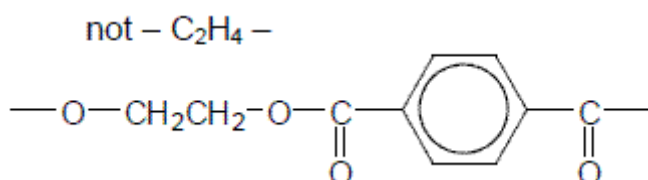
ignore errors in initial triester

First mark for 3CH₃OH

Third mark for all three esters

3

(e)



First mark for correct ester link second mark for the rest including trailing bonds

If ester link wrong, lose second mark also

2

Adv reduces landfill
saves raw materials
lower cost for recycling than making from scratch
reduces CO₂ emissions by not being incinerated
not allow cost without qualification
ignore energy uses

1

Disad difficulty/cost of collecting/sorting/processing
product not suitable for original purpose, easily contaminated

not allow cost without qualification
ignore energy uses

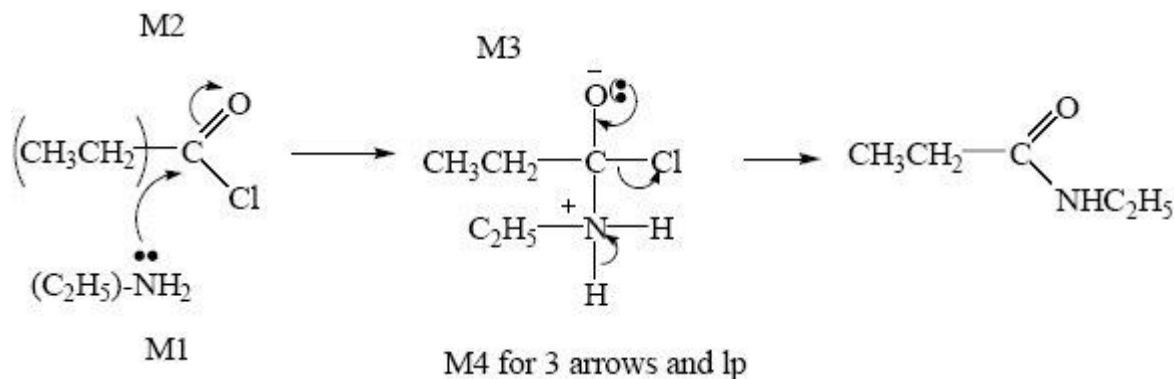
1

[19]

Q18.

(a) (nucleophilic) addition-elimination

1



4

N-ethylpropanamide

minus on NH₂ loses M1

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

+C=O loses M2

only allow M4 after correct or very close M3

lose M4 for Cl⁻ removing H⁺ in mechanism, but ignore HCl as a product

Not N-ethylpropaneamide

1

(b) CH₃CN or ethan(e)nitrile or ethanonitrile

not ethanitrile

but allow correct formula with ethanitrile

1

for each step wrong or no reagent loses condition mark

contradiction loses mark

1

Step 1 Cl₂

uv or above 300 °C

wrong or no reagent loses condition mark

1

Step 2 KCN

1

aq and alcoholic (both needed)

allow uv light/(sun)light/uv radiation

1

Step 3 H₂/Ni or LiAlH₄ or Na/C₂H₅OH

not CN⁻ but mark on
 NOT HCN or KCN + acid, and this loses condition mark
 NOT NaBH₄
 Sn/HCl (forms aldehyde!)
 ignore conditions

1

[12]

Q19.

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

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

1

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

1

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

1

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

1

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

1

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

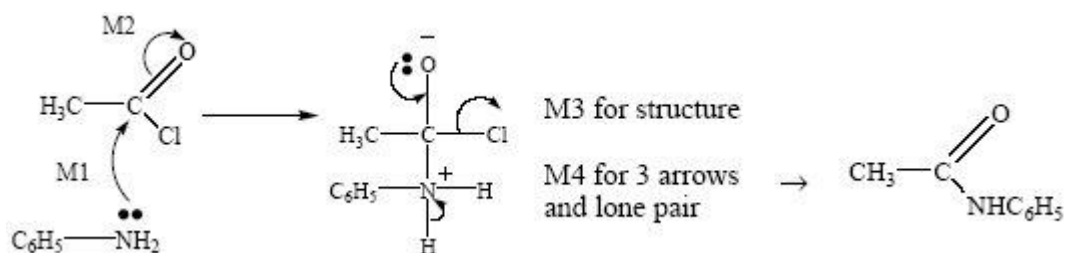
1

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

1

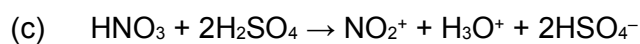
- (b) (nucleophilic) addition-elimination

1

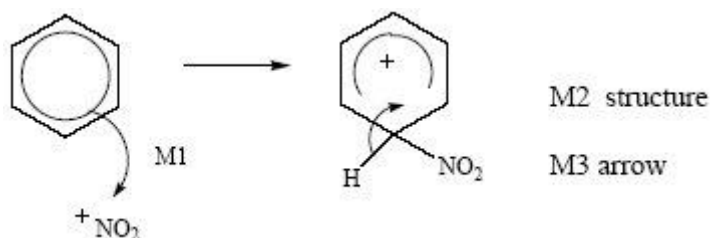


QWC (2)

4



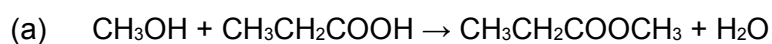
1



3

[16]

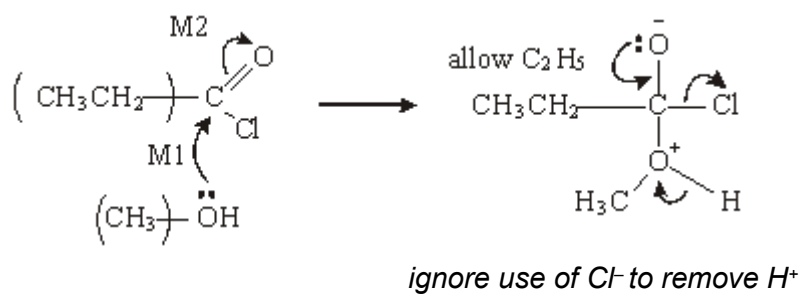
Q20.



1

- (b) (nucleophilic) addition-elimination NOT acylation

1

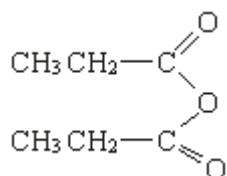


M3 for structure

M4 for 3 arrows and lone pair

4

- (c)



allow C₂H₅ and -CO₂-

allow CH₃CH₂COOCOCH₂CH₃

or (CH₃CH₂CO)₂O

1

- (d) (i) faster/not reversible/bigger yield/purer product/no(acid) (catalyst) required

1

- (ii) anhydride less easily hydrolysed or reaction less violent/exothermic
no (corrosive) (HCl) fumes formed or safer or less toxic/dangerous
expense of acid chloride or anhydride cheaper

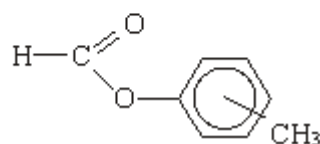
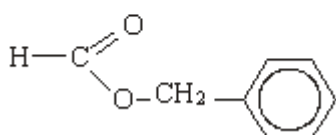
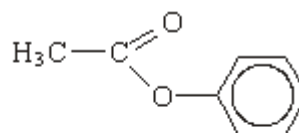
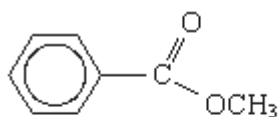
any one

1

- (e) (i) C₈H₈O₂

1

- (ii) **any two from**



Allow -CO₂- allow C₆H₅

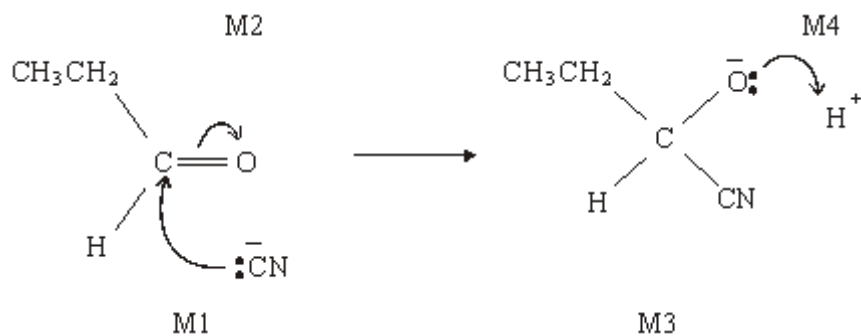
2

[12]

Q21.

(a) nucleophilic addition

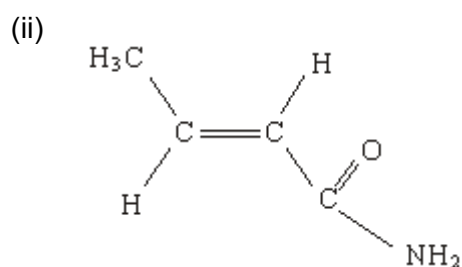
1



4

(b) (i) 2-hydroxybutanenitrile

1

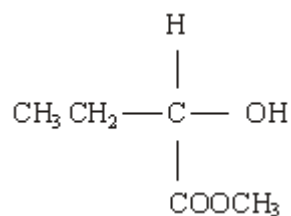


(allow 1 for amide even if not C_4H_7NO , i.e. $RCONH_2$)

(if not amide, allow one for any isomer of C_4H_7NO which shows geometric isomerism)

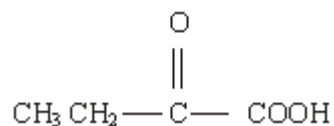
2

(c) (i)



1

(ii)



1

(iii) $CH_3CH=CHCOOH$

1

[11]

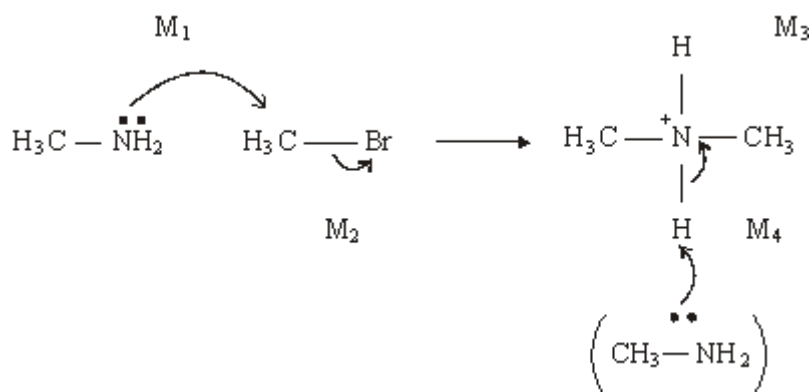
Q22.

(a) dimethylamine

1

(b) nucleophilic substitution

1



4

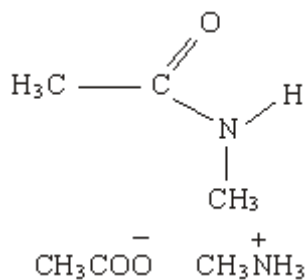
(c) quaternary ammonium salt

1

(cationic) surfactant / bactericide / detergent / fabric softener or conditioner/hair conditioner

1

(d)

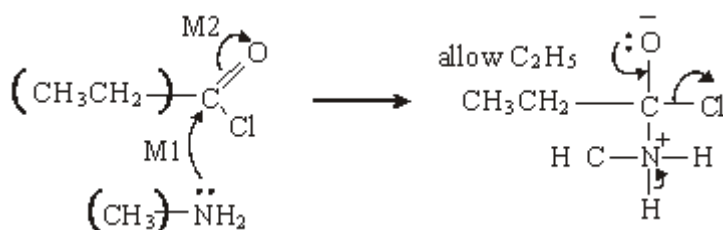
(allow CH_3COOH or $\text{CH}_3\text{COO}^- \text{NH}_4^+$)

2

[10]

Q23.

(a) (nucleophilic) addition-elimination;



(M3 for structure)

(M4 for 3 arrows and lone pair)

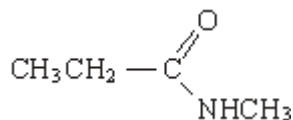
(M2 not allowed independent of M1, but allow M1 for correct attack

on C+ if M2 show as independent first.)

(+on C of C=O loses M2 but ignore δ^+ if correct)

(Cl- removing Et loses M4)

1

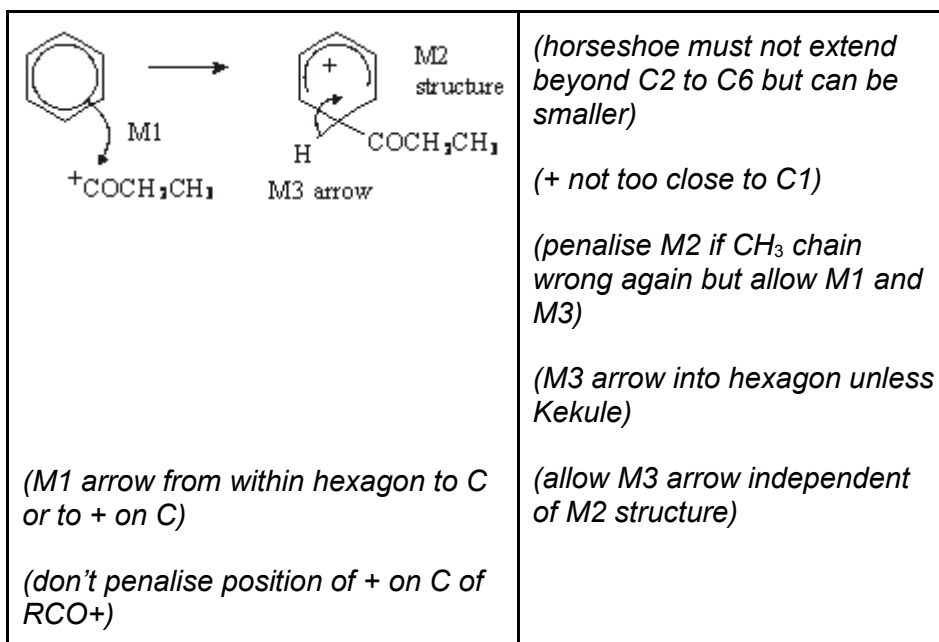


(If MS lost above for wrong C chain, do not penalise same error again here)

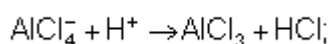
5

- (b) $\text{CH}_3\text{CH}_2\text{COCl} + \text{AlCl}_3 \rightarrow [\text{CH}_3\text{CH}_2\text{CO}]^+ + \text{AlCl}_4^-$;
 (penalise wrong alkyl group once at first error)
 (position of + on electrophile can be on O or C or outside [])
 (penalise wrong curly arrow in the equation or lone pair on AlCl_3)

1



3



(or can be gained in mechanism);

1

- (c) M1 $\text{CH}_3\text{CH}_2\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HCl}$ 1
 (penalise wrong alkyl group once at first error)

1

M2 M_r of $\text{CH}_3\text{CH}_2\text{COCl} = 92.5$ 1
 (if M_r wrong, penalise M2 only)

1

M3 moles of $\text{CH}_3\text{CH}_2\text{COCl} = 1.48/92.5 = 0.016$ 1

1

M4 moles $\text{NaOH} = 2 \times 0.016 = 0.032$ 1
 (allow for $\times 2$ conseq to wrong no of moles)

1

M5 volume of $\text{NaOH} = 0.032/0.42 = 0.0762 \text{ dm}^3$ or 76.2 cm^3 1
 (with correct units)
 (if $\times 2$ missed in M4 lose M5 also)

Q24.

- (a) (i) An appropriate alkene; $\text{CH}_3\text{CH}_2\text{CHCH}_2$ or $(\text{CH}_3)_2\text{CCH}_2$ 1
- Isomer 1 1
- Isomer 2 1
- Position isomerism 1
- Mechanism 1
- electrophilic attack and electron shift to Br (Unless H^+ used) 1
- carbocation 1
- reaction with carbocation 1
- [Allow mechanism marks for the alkene $\text{CH}_3\text{CHCHCH}_3$]*
[Allow one mark if mechanism for minor product given] 1
- (ii) An appropriate carbonyl; $\text{CH}_3\text{CH}_2\text{CHO}$ 1
- Mechanism nucleophilic attack and electron shift to O 1
- anion intermediate 1
- reaction with anion 1
- [Allow mechanism marks for the carbonyl $(\text{CH}_3)_2\text{CO}$]* 1
- Isomer 1 1
- Isomer 2 1
- Optical isomerism 1
- NB Isomer structures must be tetrahedral*
NB Penalise "stick" structures once in part (a) 1
- (b) QoL 1
- Large charge on carbonyl carbon atom due to bonding to O and Cl 1

Nucleophiles have electron pairs which can be donated

1

Equation Species

1

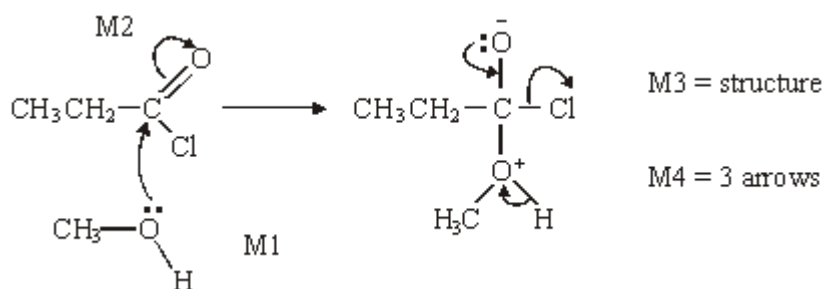
Balanced

1

[18]

Q25.

X is methyl propanoate



1

M1 for arrow and lone pair,

4

M2 for arrow
addition-elimination

1

Spectrum 2

if thinks Spectrum 1 = X can only score for structure of Y

1

Y is $\text{CH}_3\text{COOCH}_2\text{CH}_3$

1

The two marks for explanation are awarded for discussing one or more of the four peaks (not those for the CH_3 of the ethyl groups)

for stated δ values the integration or the splitting should be related to the structure: e.g. structure of **X** shows that

at δ 3.7 – 4.1 (1) spectrum of **X** should have integration 3 / singlet (1)

or

at δ 2.1 – 2.6 (1) spectrum of **X** should have integration 2 / quartet (1)

Spectrum 2 has these

[OR Spectrum 1 has

at 3.7 – 4.1 (1) quartet / integration 2 (1) so not **X**

at 2.1 – 2.6 (1) singlet / integration 3 (1) so not **X**]

2

[10]

Q26.

(a) M1 $K_p = (\text{pY})^3 \cdot (\text{pZ})^2 / (\text{pW})^2 \cdot (\text{pX})$ NB [] wrong

M2 temperature

M3 increase

M4 particles have more energy or greater velocity/speed

M5 more collisions with $E > E_a$ or more successful collisions

M6 Reaction exothermic or converse

M7 Equilibrium moves in the left

Marks for other answers

Increase in pressure or concentration allow M1, M5, M6 Max 3

Addition of a catalyst; allow M1, M5, M6 Max 3

Decrease in temperature; allow M1, M2, M6 Max 3

Two or more changes made; allow M1, M6 Max 2

- (b) (i) Advantage; reaction goes to completion, not reversible or faster

Disadvantage; reaction vigorous/dangerous
(exothermic must be qualified)

or HCl(g) evolved/toxic
or CH₃COCl expensive

NB Allow converse answers

Do not allow reactions with other reagents e.g. water
or ease of separation

- (ii) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$

$$\Delta S = (259 + 187) - (201 + 161)$$

$$\Delta S = 84 \text{ (JK}^{-1} \text{ mol}^{-1}) \text{ (Ignore units)}$$

Allow – 84 to score (1) mark

$$\Delta G = \Delta H - T\Delta S$$

$$= -21.6 - 298 \times 84/1000$$

$$= -46.6 \text{ kJ mol}^{-1} \text{ or } -46\,600 \text{ J mol}^{-1}$$

Allow (2) for – 46.6 without units

(Mark ΔG consequentially to incorrect ΔS)

(e.g. $\Delta S = -84$ gives $\Delta G = +3.4 \text{ kJ mol}^{-1}$)

Q27.

- (a) Cyclohexane evolves
- 120 kJ mol^{-1}

$\therefore$ (expect triene to evolve) 360 kJ mol^{-1} (1) or 3×120

$$360 - 208 = 152 \text{ kJ (1) NOT 150}$$

152 can score first 2

QofL: benzene lower in energy / more (stated) stable (1)

Not award if mentions energy required for bond breaking

due to delocalisation (1) or explained

4

- (b) (i) phenylamine weaker (1)

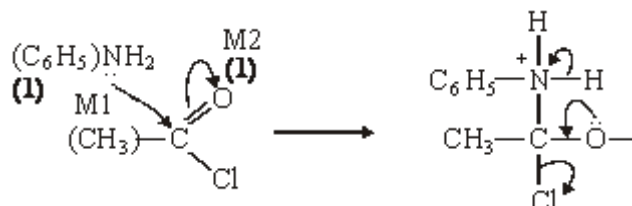
if wrong no marks

lone pair on N (less available) (1)

delocalised into ring (1) or "explained"

3

- (ii) addition – elimination (1)



structure (1) M3

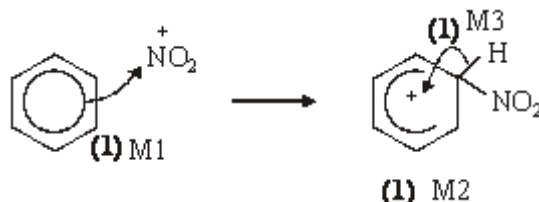
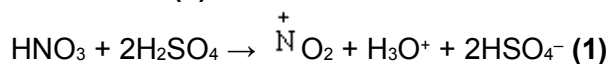
3 arrows (1) M4

N-phenyl ethanamide (1)

6

- (iii) conc
- HNO_3
- (1)

conc H_2SO_4 (1)



(1) M2

6

- (iv) peptide / amide (1)

NaOH (aq) (1)

HCl conc or dil or neither
H₂SO₄ dil NOT conc
NOT just H₂O

2

Notes

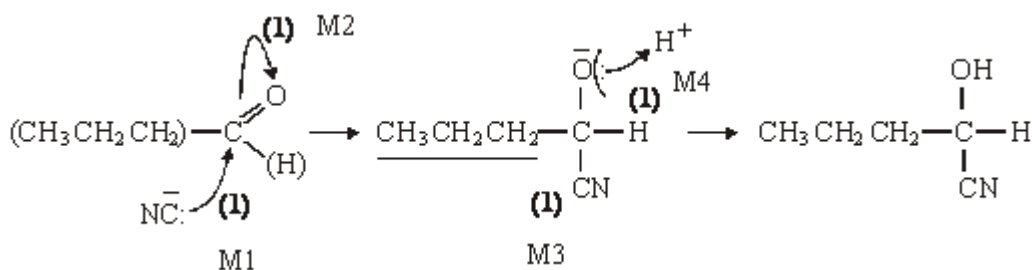
- (a)
- 360 or 3×120 or in words (1);
 - 152 NOT 150 (1); (152 can get first two marks)
 - **Q of L** benzene more stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene (1);
 - delocalisation or explained (1)
- (b) (ii) or N-phenylacetamide or acetanilide
mechanism: if shown as substitution can only gain M1
if CH₃CO⁺ formed can only gain M1
lose M4 if Cl⁻ removes H⁺
be lenient with structures for M1 and M2 but must be correct for M3
 alone loses M2
- (iii) **No marks for name of mechanism in this part**
if conc missing can score one for both acids (or in equation)
allow two equations

allow $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$
ignore side chain in mechanism even if wrong
arrow for M1 must come from inside hexagon
arrow to NO₂⁺ must go to N but be lenient over position of +
+ must not be too near "tetrahedral" Carbon
horseshoe from carbons 2-6 but don't be too harsh
- (iv) reagent allow NaOH
HCl conc or dil or neither
H₂SO₄ dil or neither but not conc
not just H₂O

[21]

Q28.

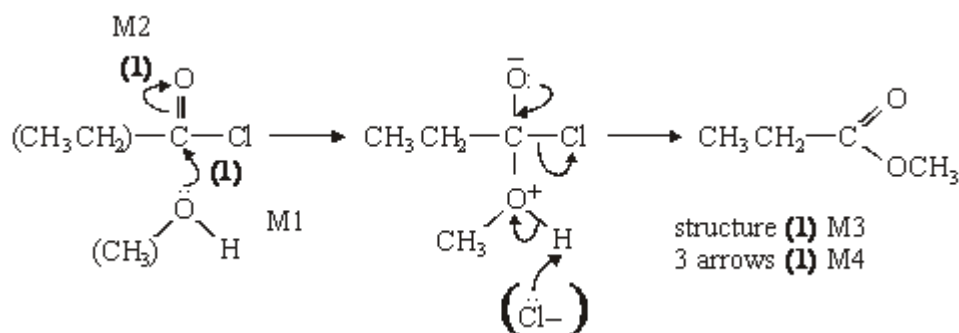
(a) Mechanism



Allow C₃H₇ if structure shown elsewhere
penalise HCN splitting if wrong

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

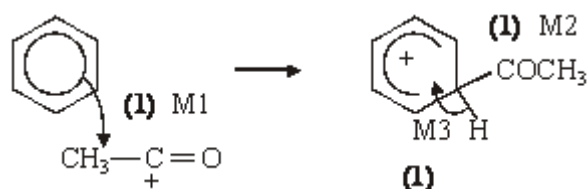
(b) *Mechanism*



Name of organic product: methylpropanoate (1)

(c) (i) (1) $\text{CH}_3\text{CO}(\text{l})^+$ (1)

(ii)



Notes

(abc) extra curly arrows are penalised

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

(a)/(b) $\text{C}=\text{O}$ alone loses M2 but can score M1 for attack on C⁺, similarly $\text{C}-\text{Cl}$

(a) allow 2-hydroxypentanitrile or 2-hydroxypenta(ne)nitrile ... pentynitrile

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

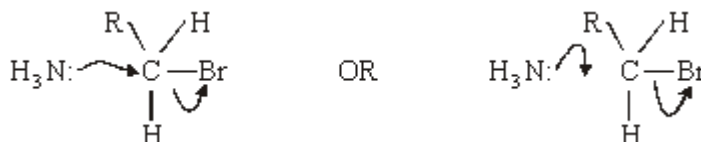
(c) (i) allow formula in an "equation" (balanced or not)
be lenient on the position of the + on the formula

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

[14]

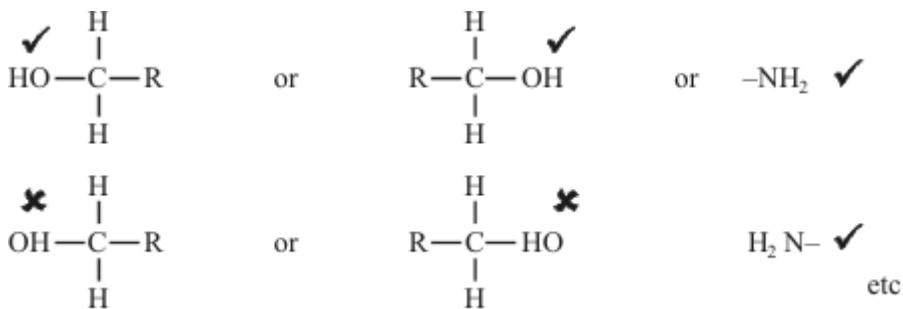
Organic points

(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH₃- or -CH₃ or  or CH₃
or H₃C-

Q29.

- (a) (i) Moles NaOH = $mv/1000 = 1.50 \times 72.5/1000 = 0.108$ to 0.11 **(1)**
 Moles of ethanoic acid at equilibrium = moles sodium hydroxide **(1)**
 Moles ester = moles water (=moles acid reacted) **(1)**
 $= 0.200 - 0.108 = 0.090$ to 0.092 **(1)**
 Moles ethanol = $0.110 - 0.091 = 0.018$ to 0.020 **(1)**
 $K_c = [\text{Ester}] [\text{Water}] / [\text{Acid}] [\text{Alcohol}]$ **(1)**

Allow if used correctly

$$= (0.091)^2 / 0.109 \times 0.019 = 3.7 \text{ to } 4.9 \text{ (1)}$$

Ignore units

NB *Allow the answer 4 one mark as correct knowledge*

7

- (ii) Similar (types) of bond broken and made **(1)**
Same number of the bonds broken and made **(1)**
any number if equal
NB *If a list given then the total number of each type of bond broken and made must be the same*

2

- (b) (i) (Weak) dipole-dipole attraction between HCl molecules **(1)**
 (Strong) **hydrogen bonds** between CH₃COOH molecules **(1)**
NB *Ignore van der Waals forces*

2

- (ii) Ethanoic anhydride is

cheap compared to ethanoyl chloride (1)

less corrosive than ethanoyl chloride or HCl evolved (1)

reaction less violent or vigorous or exothermic or dangerous
or safer to use (1)

less vulnerable to hydrolysis (1)

reaction more easily controlled (1)

Max 2

[13]

Q30.

C

[1]

Examiner reports

Q1.

- (a) This was a straightforward question on a familiar topic and many good students (46.5%) scored full marks. However, some drew structures, such as the horseshoe in the mechanism, with insufficient care and consequently failed to gain marks. Others omitted charges on the ions in the equation (especially on AlCl_4^-), or in the mechanism did not draw the + on the carbonyl carbon in the electrophile.
- (b) In this question, although some students struggled with the name, a number failed to gain the mark due to a failure to label 1-phenyl in an otherwise correct name. Most identified a correct reagent but “electrophilic addition” and “reduction” were frequent wrong answers for the name of the mechanism.
- (c) This question was generally answered well, especially the name of the mechanism and the structure of the ester. A common error was to give the name of the product, i.e. ‘HCl gas’, rather than an observation as required, or alternatively to describe this as a ‘white precipitate’.

Q2.

- (a) The zwitterion was drawn correctly by all except the weakest students.
- (b) The structure of the negative ion formed by serine in alkali was less well known and occasionally the response showed a hydrogen removed from the alcohol group, as well as from the acid.
- (c) Although the questions asked for ‘both dipeptides’, several students drew only one. The amide link was also occasionally drawn with an extra oxygen atom included, and occasionally cysteine was used instead of serine.
- (d) This question was well answered and 25% of students scored all six marks. The name of the organic product was the most common mark lost, closely followed by slips in the third or fourth marks in the mechanism.

Q3.

- (a) This part, and others in this question, illustrate the importance of students paying attention to **why** certain techniques and processes are used during practicals. The role of anti-bumping granules was not as well understood as expected, with only 30% of students gaining this mark. Incorrect suggestions included that they slow the reaction down by preventing the reactant particles from bumping into each other.
- (b) This proved to be an easy question for most, although there were issues with the layout of the calculation; it was not always clear which calculation related to which reactant.
- (c) Nearly 60% of students gained this mark but a lack of specific clarity cost many dearly. Many students apparently did not retain an awareness of the context of a question as they worked through the stages. They did not appear to recall, from the stem of the question, that the reaction was between NaOH and ethyl benzoate. This recall should have enabled students to make the specific statement that the excess of sodium hydroxide was to ensure that all the ethyl benzoate would react.
- (d) Answers here often incorrectly referred to the ‘control’ of the temperature rather than

recognising the risk of flammability of organic reagents. Clarity is again key, because any suggestion that NaOH is flammable is incorrect.

- (e) As was also evident in part (f), some students thought that reflux is a separation method. A specific answer was again the key here, with a need to mention the fact that reactant/organic **vapours** are returned to the reaction mixture. Suggestions that reflux prevents vapour forming were incorrect.
- (f) This was answered best by students who used structural or partial skeletal formulas. Many students, who attempted to use molecular formulas, often miscounted the number of hydrogens or carbons. Care was needed to avoid any suggestion that there is an O–Na bond in sodium benzoate.
- (g) As mentioned previously, this proved to be the trickiest question on the paper, with only 1% of students earning both marks. Most could state that sodium benzoate is ionic – although there were also many incorrect references to it being ‘polar’ or ‘a molecule’. However, a proper description of why benzoic acid is insoluble was beyond most students. Many stated that it is non-polar, while others suggested that its ability to hydrogen-bond with itself is what prevents it dissolving. Very few were able to clearly explain that, despite the polarity (and hence the ability to form hydrogen bonds with water), the large non-polar benzene ring prevented dissolving.
- (h) About a third of students earned 4 or more marks here, but about the same number failed to score. Despite a statement in the stem that benzoic acid is a solid, many answers referred incorrectly to methods based on distillation and/or solvent extraction. Some answers implied that a solid would be expected to run through the tap of a separating funnel! For those students who correctly recognised that recrystallization was the correct method, there was often confusion in the order of the steps, which prevented potentially good answers gaining full marks. An example seen quite often was the suggestion that the solid obtained after cooling/crystallisation should be washed **before** filtering. The steps most often missing were the need for hot filtration after dissolving the impure solid in hot solvent, and the final wash and dry after Buchner filtration.
- (i) This was another tricky question, with only 10% of students earning full marks. It seemed that many were thrown by the realisation that the answer was over 100%, with many students responding by doing the percentage calculation the wrong way round, because they seemed to feel that the answer must be less than 100%. Relative molecular masses were often calculated incorrectly despite that for ethyl benzoate being given in the stem. The M_r of ethyl benzoate was sometimes used in place of the M_r of benzoic acid.

Q6.

The IUPAC name in part (a)(i) proved harder than expected with answers including 1-chloro or ethyl. The mechanism in part (a)(ii) was well known with over half of students gaining full marks. There was a wide range of answers to part (d) with both the number of hydrogens and the overall M_r proving harder than expected, but, even so, nearly half of all students scored both marks. Many students knew (e) was tertiary but some thought it was an amide rather than an amine.

Part (f)(i) was generally well done and in the correct responses there was a fairly even distribution between those describing why b is a stronger base or why a is a weaker base. Part (f)(ii) proved more difficult and only the best students scored any marks. The term salt was given in the question and so just that link was not credited. Few stated that the ionic character of the salt would make it more water-soluble than lidocaine itself.

Q7.

The equation in part (a)(i) was fairly well written. By comparison, few students could name the ester correctly. The more common errors in the equation were to give a straight chain alkyl group in the ester, or to give the second product as water or to leave it out altogether. In part (a)(ii), the nucleophilic addition-elimination mechanism was well done with over half of the students scoring full marks.

In part (b)(i), the mark for 3NaOH was frequently scored, whereas the mark for the right hand side of the equation was often lost mainly due to mistakes in the salts, such as an incorrect number of hydrogen atoms, a covalent bond from O to Na, or covalent bonds between the three salts. Almost half of the students gained the mark in part (b)(ii). Those who lost it gave the carboxylic acid instead of the methyl ester or misread the question and calculated the Mr of the molecule rather than giving its formula.

Q8.

The skill of chemical communication is one which is being assessed here. Parts (a)(i) and (ii) were frequently well done with, occasionally the usual difficulty with what is expected for precision – this cannot be ignored by centres. Many good answers were seen for part (b)(i) but only the best students got full marks with parts of the detail missing. There appeared, for some centres, to be an obsession with washing, even ‘washing solutions’! Part (b)(ii) was well answered by many, especially where they had carried out the procedure but M3 was occasionally lost through a lack of clarity regarding the required ‘match’ with data values. Part (b)(iii) was well answered but part (c) was marked too generously; again a lack of clarity was often evident and centres were frequently too generous, misapplying the Marking Guidelines e.g. HCl is not toxic.

Q9.

The nucleophilic addition-elimination mechanism in part (a)(i) presented a real challenge to many students, who were confused by the cyclic nature of the product, failed to identify the correct nucleophile and suggested either separate nucleophiles such as H₂O, CH₃OH and OH⁻ or alternatively loss of the proton from the OH group before nucleophilic attack. Most students gave the correct range for the carbon atom labelled **b**, but often the range for the carbon atom labelled **a** was given as 160–185 as for a carbonyl carbon. In part (a)(ii), the repeating unit for the polyester was answered well although some students gave twice the repeating unit.

The distinguishing test in part (b) was well done, although a significant number of students thought that substance **K** was an acid and wrongly suggested NaHCO₃ or Na₂CO₃ to distinguish between the compounds. It was common for students to fail to see the symmetry of **J** and so to predict, incorrectly, three peaks in its proton n.m.r. spectrum. Five peaks was a common incorrect answer for **K**, suggesting that students had misread the question and given the ¹³C n.m.r. result.

Part (c) of this question proved to be very challenging and fewer than 10% of students scored full marks. Isomer **Q** was found particularly difficult where many students omitted one of the O atoms from their suggested structure. Other common errors included missing the double bond in **L**, giving the structure of **P** as the structure of **N** (which suggests a failure to recognise that optical isomerism is a form of stereoisomerism) or writing an unbranched carbon chain for the acid **N**. Answers to part (c) were often very badly presented, with a great deal of crossing out, duplication of answers and poor labelling of structures.

Q10.

- (a) This part proved very challenging, with many students failing to draw apparatus for filtering under reduced pressure. Of those who did choose appropriate equipment, it was common to see sealed flasks and funnels, rendering them incapable of being used.
- (b) About half of the students were able to state a suitable piece of apparatus in this part. However, only a very small number were able to describe clearly the process of heating slowly near to the melting point. A number of very vague answers were seen in response to this question, as well as simple restating of the question itself.

Q11.

In this Question, a number of students spoiled their answer by including sodium hydroxide in the test reagent. The use of water was occasionally allowed even though it was specifically disallowed in the Marking Guidelines.

Q12.

In part (a)(i), only the most able could write a correct overall equation and name the product correctly. Marks awarded for the electrophilic substitution mechanism were high although some students were careless in their drawing of the Wheland intermediate, particularly the position of the + in the hexagon.

The definition of a nucleophile was not well answered in part (b). Many realised that nucleophiles have a lone pair but failed to mention that they could donate them; others offered a description in terms of attraction to an electron rich area.

The structure of the organic product was well attempted but many failed to recognise it as an acid anhydride, often suggesting that it was an ester.

Q13.

In part (a), the mechanism was frequently correct and well presented, but some students lost a mark by writing a minus charge on the oxygen of methanol. Methyl ethanoate was a common wrong name for the product ester.

There were few correct answers to part (b)(i); IUPAC nomenclature requires an 'e' before the numbers. Many correctly identified the diacyl chloride in part (b)(ii) but some failed to give its displayed formula. Although hydrolysis was often correctly identified, part (b)(iii) proved to be difficult, with many offering the breaking of peptide bonds as an explanation and very few identifying attack by the hydroxide ion on the electron deficient carbon as a contributory factor. Part (c)(i) was very well done although a few lost the mark by drawing incomplete structures, notably by omitting the oxygen in the OH of the acid group so giving an aldehyde.

Despite the question in part (c)(iii) stating 'other than cost', many students still gave the answer that the anhydride is cheaper. Another common wrong answer was to describe the loss of chlorine rather than hydrogen chloride. Part (d) was correctly answered by half of the students; some of the others lost the mark by careless omission of an oxygen atom and so drew a ketone rather than an ester.

Only the weakest students failed to answer parts (e)(i) and (e)(iii) correctly, but only the top 20% were able to deduce the number of ^{13}C peaks correctly in part (e)(ii).

Q14.

This Question discriminated well between students that could express scientific ideas

logically, concisely and accurately and students who could not. The question would have discriminated well if some schools and colleges had been less keen on awarding a mark for incomplete answers or answers which were disallowed in the Additional Guidance. A vague reference to removing impurities was often credited twice. Schools and colleges are reminded that when the answer in the Marking Guidelines includes words which have been underlined, **all** of these words, or their very close equivalents, **must** be present if an answer is to be credited.

Q15.

These mechanisms were well done and clearly presented with about a third of students scoring full marks. However, many struggled to name both compounds correctly. Propanamide proved especially difficult, with incorrect names based on aminoketone appearing very frequently. There were some good answers to part (c), but many others involved comments about ammonia not being attracted to the benzene ring rather than actively being repelled by it. 'Ammonia is a nucleophile' was another frequent wrong answer.

Q16.

Questions that require identification of a reagent and a subsequent observation defeat many candidates. Providing the reagent in the rubric for the question did not seem to help and correct answers to this Question were rare. Most candidates realised that one of the reactions would produce a white precipitate but often chose the wrong one. The production of a silver mirror was often given.

Overall, the scheme seems to have gone well once again. Given the pressures on centres to deliver the teaching programme, this was a very positive and encouraging outcome. Centres are once again warmly commended for their efforts.

Q17.

A few candidates were unsure of the names of the esters involved and confused butyl ethanoate with ethyl butanoate. In parts (a) and (b) a common error was the failure to balance the equations due to the omission of water or ethanoic acid respectively. Weaker candidates were also unsure of the structure of ethanoic anhydride.

The mechanism in part (c) was well answered although several omitted to give its name. The reaction in part (d) proved unfamiliar to many candidates; some attempted to answer the question in terms of alkaline hydrolysis of the ester to form soap rather than the reaction with methanol to form the mixture of methyl esters which make up biodiesel. The repeating unit was well answered in part (e).

Q18.

In part (a), a significant number missed out the name of the mechanism and also could not name the product correctly. However, better candidates scored well in this question.

Part (b) required synoptic understanding and knowledge of some reactions from AS as well as knowledge of the chemistry of amines from A2. A surprising number could not give the correct reagent for the formation of CH_3Cl from methane. Although many realised that the second step in the synthesis required use of a cyanide to increase the carbon chain from one to two, many confused the use of HCN in nucleophilic additions with the use of aqueous/alcoholic KCN without any acid in the nucleophilic substitution needed here.

Q20.

Good candidates were able to score high marks in this question.

The equation in part (a) was well answered; leaving out H_2O was the most common error. The mechanism in part (b) was well done by many, although several weaker candidates persist in writing a negative charge as well as a lone pair on nucleophiles such as methanol used here. Incorrect structures for propanoic anhydride were common in part (c); many contained only three carbon atoms in total. By contrast, most candidates were able to answer part (d) correctly. In part (e)(i) many did not understand the meaning of the term “molecular formula” and wrote semi-structural formulae instead. However many correct structures were written in part (e)(ii).

Q21.

As usual, better candidates find organic mechanisms straightforward and many good answers were seen to part (a). In part (b)(i) the name 2-hydroxybutanenitrile, was usually given correctly. The abbreviation 2-hydroxybutanenitrile was not allowed.

The structure of the isomer of $\text{C}_4\text{H}_7\text{NO}$ was found difficult. It was possible to score one mark for a structure with the correct molecular formula which showed geometric isomerism. Sadly many candidates did not recognise that an acyl chloride reacts with ammonia form an amide.

In part (c), there were many pentavalent carbons shown in the structures drawn, especially in part (ii). The elimination of water in part (iii) to form an alkene was the least well-known reaction.

Q22.

A disappointingly small number of candidates could name the secondary amine correctly in part (a), although the mechanism was well answered by the better candidates. The name quaternary ammonium salt was well known and many uses for such compounds were allowed. Part (d) was found difficult by many candidates who seemed unfamiliar with anhydrides and their reactions.

Q23.

The better candidates often gained full marks in part (a). The most common errors were similar to those described in Question 3(a) above. In part (b), despite the request to write equations to show the role of aluminium chloride, many drew a mechanism often containing incorrect curly arrows and were penalised. The electrophilic substitution mechanism was generally well answered although careless drawing of the electrophile with wrong position of the + charge often led to incorrectly linked COCH_2CH_3 side chains, with CH_3 or O joined to benzene ring. Many failed to write an equation for the regeneration of the AlCl_3 catalyst. In part (c), few realised that hydrolysis of propanoyl chloride forms both propanoic and hydrochloric acids, both of which react with sodium hydroxide. Hence the most common answer was half the correct value. A disappointing number also failed to calculate the correct M_r of propanoyl chloride, the formula for which was given at the start of the question.

Q24.

Part (a)(i) was well answered. Many candidates chose a correct alkene, gave two structural isomers formed in the reaction with HBr and named the type of structural isomerism. Candidates who chose an incorrect alkene were able to score three marks for a correct mechanism. In (a)(ii) choosing a carbonyl compound with the molecular formula

$\text{C}_3\text{H}_6\text{O}$ which forms two isomers when HCN is added proved more difficult and many candidates gave the incorrect carbonyl $(\text{CH}_3)_2\text{CO}$. Marks were again allowed for a correct mechanism even when the carbonyl was incorrect. Candidates were only allowed to score a mark for stating that the isomers formed were optically active if the isomers given had an asymmetric carbon. As square planar molecules are not optically active, structure marks were only awarded when isomers were shown as tetrahedral arrangements. Almost all candidates were able to write an equation for a nucleophilic addition-elimination reaction of ethanoyl chloride but equations involving NH_3 were only given full marks if NH_4Cl rather than HCl was given as a product. Many candidates omitted to state the polarising effects of both the oxygen and the chlorine atoms when explaining why the reactions occur readily. Most also failed to state that nucleophiles are able to react because they have a lone electron pair which they can donate.

Q25.

Many candidates were able to name ester **X** correctly but fewer could give the correct name for the mechanism involved in the formation of **X** from an acid chloride and an alcohol. Too many candidates also forgot that the mechanism initially involves addition in which the $\text{C}=\text{O}$ bond becomes $\text{C}-\text{O}$ and then, subsequently, the $\text{C}=\text{O}$ bond is reformed in the second step which involves elimination. Better candidates were able to state that Spectrum 2 was that of ester **X**, but many did not explain their deduction clearly. Both spectra contain a peak in the δ range 3.7 - 4.1 which could apply to an ester, and this statement alone was insufficient. It was necessary to state that for **X**, the absorption in this region must be a singlet or have an integration value 3. Despite the statement in the question that **Y** was "an isomeric ester", many suggestions for the structure of **Y** were not those of esters.

Q26.

Many candidates gave a correct expression for the equilibrium constant, K_p , for the reaction given in part (a). Some, who gave correct indices, lost a mark as they included square brackets, which are specific used to indicate concentration, in their expression. Identifying the one change which would increase the rate of reaction and decrease the value of K_p proved challenging but part marks were awarded for answers which addressed either of the two required changes. Candidates who gave more than one change of condition were able to score one mark for a correct K_p expression. There were many vague answers to part (b)(i), some of which assumed there were other reactants present with the most common example being water in Reaction 2. By contrast, (b)(ii) was very well answered with many candidates scoring full marks. Most candidates now remember to use either kJ mol^{-1} or J mol^{-1} throughout these calculations but a small number still failed to do this. Consequential marks were awarded in each part of the calculation.

Q27.

In part (a), not all candidates noted the requirement in the question to "Use the data". The numerical difference of 152 kJ mol^{-1} between the expected enthalpy of hydrogenation of -360 kJ mol^{-1} and the actual value of -208 kJ mol^{-1} was rarely noted. Weaker candidates also thought that the data given was of the energy required to cause the reaction, rather than that evolved in the reaction. In part (b), weaker candidates muddled the expected addition-elimination reaction of an acid chloride and an amine with a Friedel Craft's substitution in the benzene ring and frequently gained no marks for the section. The correct name for the product, N-phenylethanamide was rarely seen. Part (c) was better answered; most candidates were able to discuss nitration correctly and the mechanism was better answered than that in part (b)(ii). The amide or peptide link was not always named correctly in part (iv) and many did not state that acidic or alkaline hydrolysis is required to break the bond.

Q28.

In organic mechanisms, a curly arrow must start at a lone pair or at a bond. This idea was still forgotten by some candidates. In part(a), several used a lone pair on the nitrogen atom rather than one on the carbon of the cyanide ion. A few confused the nucleophilic addition in part (a) with the addition-elimination in part (b) and tried in part (a) to reform a carbon to oxygen double bond. An appreciable number thought that the name of the product was a propanenitrile instead of 2-hydroxypentanenitrile. In both parts (a) and (b) the C=O bond should not be shown breaking before the nucleophile attacks. The ester was often correctly named as methyl propanoate but many other suggestions were also seen. Part (c) discriminated well. Only the better candidates were able to identify the correct electrophile, join it correctly to the benzene ring, draw the correct intermediate and show the loss of H⁺ correctly.

Q29.

The calculation of the equilibrium constant, K_c , required in part (a)(i) was generally well done. The most common error was made by candidates who subtracted the equilibrium moles of ethanoic acid from the initial moles of alcohol when calculating the moles of alcohol at equilibrium. Consequential marks were awarded after any arithmetic error. In answer to (a)(ii), most candidates recognised that similar bonds were being broken and made during the formation of the ester, but not all stated that the same number of these bonds was involved. Part (b)(i) most candidates stated correctly that hydrogen bond between ethanoic acid molecules explains why it is a liquid at room temperature but rather less candidates referred to the weaker dipole-dipole attractive forces between molecules of hydrogen chloride. Almost all candidates were able to give two advantages of using ethanoic anhydride rather than ethanoyl chloride in the manufacture of aspirin.