1

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	**B** (i) and (iii) only	**C** (ii) and (iv) only	**D** (iv) alone

Products from the acid hydrolysis of the ester $CH_3CH_2COOCH_2CH_3$ include

(i) CH_3CH_2COOH

(ii) CH_3COOH

(iii) CH_3CH_2OH

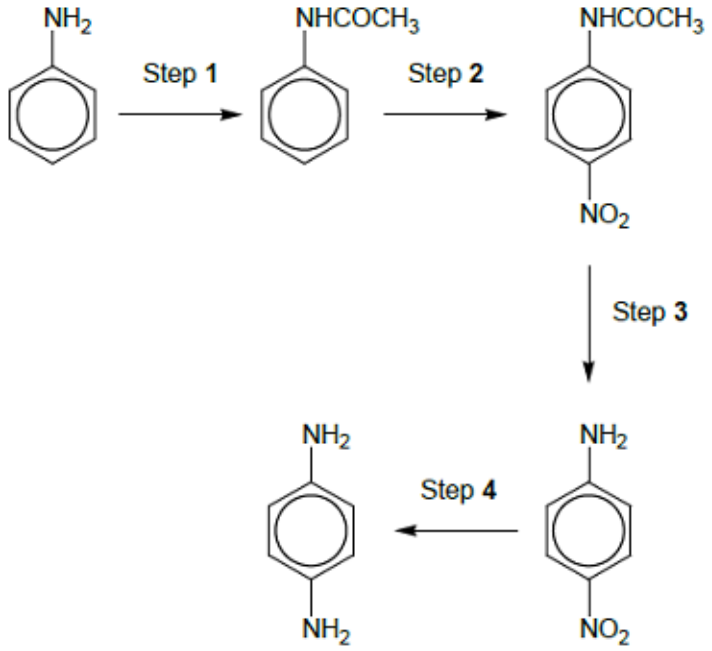
(v) $CH_3CH_2CH_2OH$

(Total 1 mark)

2

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.

.....

.....

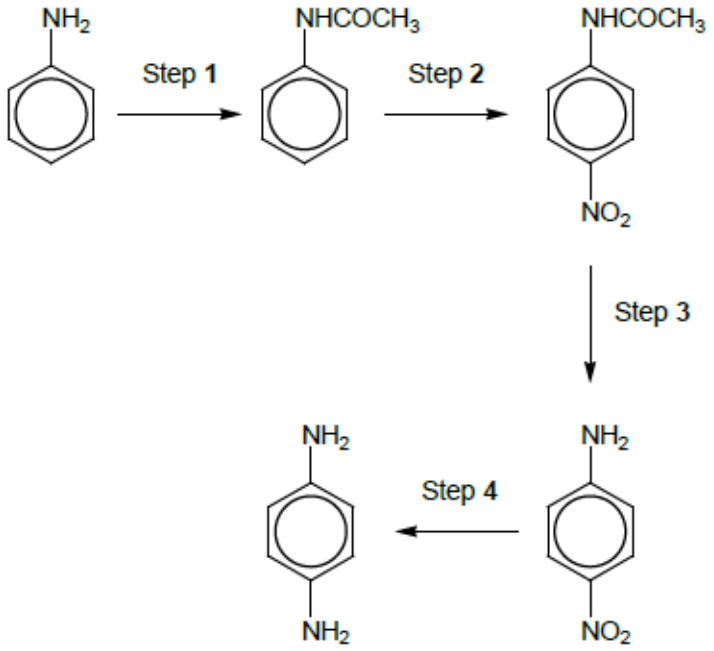
.....

.....

.....

(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)

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

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

Method **1** alcohol + acid anhydride

Method **2** alcohol + acyl chloride

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

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

Equation

.....

IUPAC name of the ester .....

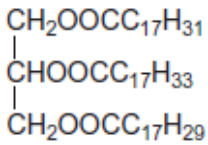
(2)

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

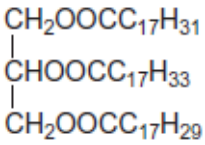
Outline a mechanism for this reaction.

(4)

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



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



.....

(2)

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

.....

(1)

(Total 9 marks)

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

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

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

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

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

Show your working.

.....

.....

.....

.....

.....

.....

.....

(3)

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

Calculate the percentage yield for the reaction.

.....

.....

.....

.....

(1)

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

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

(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.

.....

.....

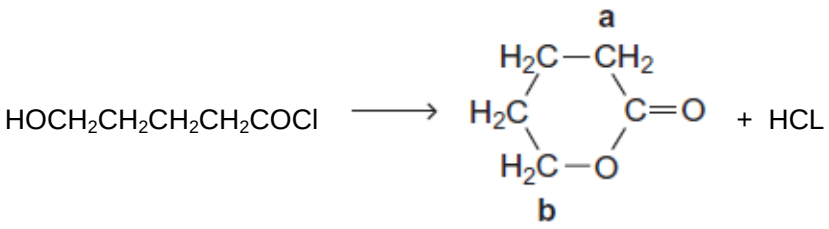
.....

(2)
(Total 15 marks)

5 This question is about some isomers of $C_5H_8O_2$

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

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



H

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

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(7)

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

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

.....

.....

.....

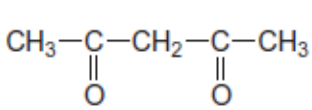
.....

.....

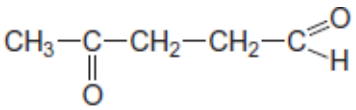
(2)

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

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



J



K

.....

.....

.....

.....

.....

.....

.....

.....

(5)

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

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

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

6 Ethanoic acid, propyl ethanoate and propan-1-ol are all colourless liquids. Esters do **not** give a positive result with any of the usual tests for functional groups.

State how you could use chemical tests to show the presence of ethanoic acid and propan-1-ol in a mixture of the acid, the alcohol and the ester.

.....

.....

.....

.....

.....

.....

.....

.....

(Total 4 marks)

7 (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.

.....

.....

.....

.....

(2)
(Total 4 marks)

8 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)

9 Esters are produced by the reaction of alcohols with other esters and by the reaction of alcohols with carboxylic acids.

(a) The esters which make up biodiesel are produced industrially from the esters in vegetable oils.

(i) Complete the equation for this formation of biodiesel.

....

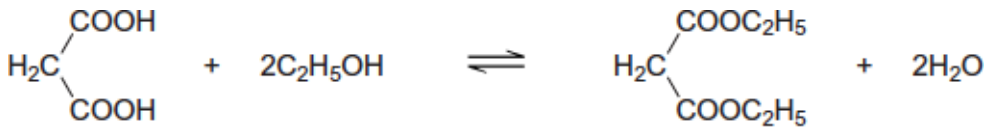
(2)

(ii) Write an equation for the complete combustion of $C_{17}H_{35}COOCH_3$.

.....

(2)

(b) The ester commonly known as diethyl malonate (**DEM**) occurs in strawberries and grapes. It can be prepared from acid **A** according to the following equilibrium.



A **DEM**

(i) A mixture of 2.50 mol of **A** and 10.0 mol of ethanol was left to reach equilibrium in an inert solvent in the presence of a small amount of concentrated sulfuric acid.

The equilibrium mixture formed contained 1.80 mol of **DEM** in a total volume, *V* dm^3, of solution.

Calculate the amount (in moles) of **A**, of ethanol and of water in this equilibrium mixture.

Moles of **A** .....

Moles of ethanol .....

Moles of water.....

(3)

(ii) The total volume of the mixture in part (b)(i) was doubled by the addition of more of the inert solvent.

State and explain the effect of this addition on the equilibrium yield of **DEM**.

Effect .....

Explanation .....

.....

(2)

(iii) Using **A** to represent the acid and **DEM** to represent the ester, write an expression for the equilibrium constant K_c for the reaction.

.....

.....

(1)

(iv) In a second experiment, the equilibrium mixture was found to contain 0.85 mol of **A**, 7.2 mol of ethanol, 2.1 mol of **DEM** and 3.4 mol of water.

Calculate a value of K_c for the reaction and deduce its units.

Calculation.....

.....

.....

.....

.....

.....

.....

.....

Units.....

.....

(3)
(Total 13 marks)

10 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)

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

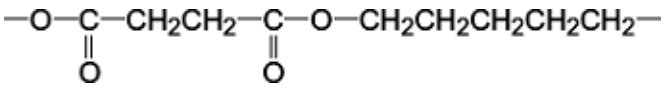
(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product .....

(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 .....

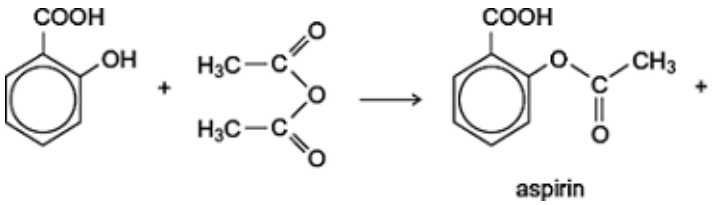
.....

.....

.....

(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 .....

.....

.....

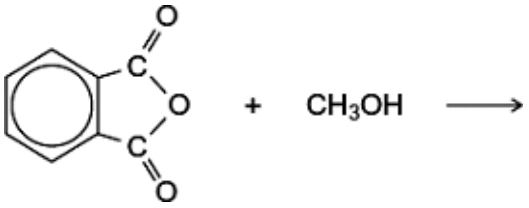
Advantage 2 .....

.....

.....

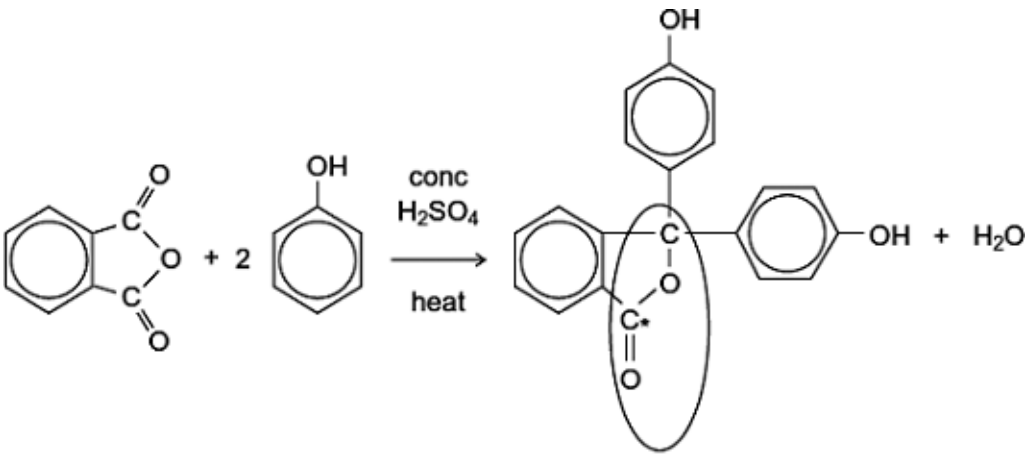
(2)

(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)

12 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 .....

.....

Filtered hot .....

.....

Cooled in ice .....

.....

Washed with cold water .....

.....

(Total 5 marks)

13 Salicylic acid, $C_6H_4(OH)COOH$, reacts with magnesium to produce magnesium salicylate and hydrogen.

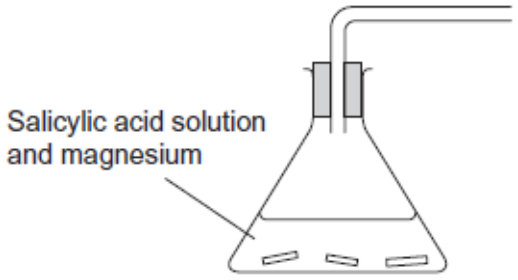
(a) Complete the equation for this reaction.

$C_6H_4(OH)COOH$

(1)

(b) In an alternative method for determining percentage purity, a student reacted a solution of salicylic acid with an excess of magnesium and collected the hydrogen gas that was released.

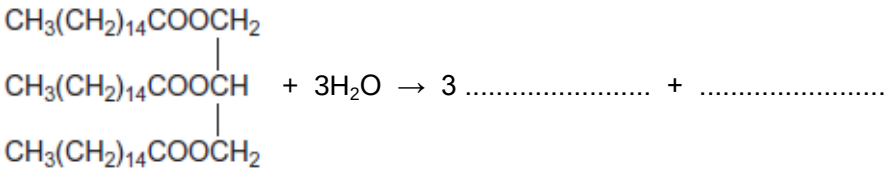
Complete the diagram below to show an apparatus that could be used to collect and measure the volume of hydrogen gas produced.



(1)
(Total 2 marks)

14 The slowing down of chemical processes is important in food storage. Over time, fats may become rancid. This involves the formation of compounds that have unpleasant odours and flavours within the food.
Hydrolysis of fats is one way in which rancid flavours are formed. Fats break down to long-chain carboxylic (fatty) acids and glycerol.

(a) Complete the right-hand side of the equation below to show how hydrolysis affects the molecule of fat shown.



(2)

(b) Other than by cooling, suggest **one** method that would decrease the rate of hydrolysis of fats.

.....

.....

.....

(1)

(c) Food can also acquire unpleasant flavours when the fatty acids, produced by hydrolysis of fats, are oxidised by air. This oxidation occurs by a free-radical mechanism.
Chemicals called anti-oxidants can be added to food to slow down the oxidation.
Suggest why anti-oxidants are **not** regarded as catalysts.

.....

.....

.....

.....

(2)

(d) A student investigated the extent of hydrolysis in an old sample of the fat in part (a).
The carboxylic acid extracted from a 2.78 g sample of this fat (M_r = 806.0) reacted with 24.5 cm^3 of a 0.150 mol dm^{-3} solution of NaOH.
Calculate the percentage of the fat that had hydrolysed.
Show your working.

.....

.....

.....

.....

.....

.....

.....

.....

(4)
(Total 9 marks)

15 A student prepared a sample of aspirin (melting point 135 °C) in the laboratory and attempted to purify it by recrystallisation. To check the purity of the aspirin the student determined its melting point.

(a) State **two** observations, during this melting point determination, that would indicate that the sample is **not** pure.

Observation 1 .....

.....

Observation 2 .....

.....

(2)

(b) Suggest why a pure sample of aspirin may sometimes appear to melt at a temperature different from 135 °C.

.....

.....

(1)
(Total 3 marks)

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

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

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

(6)

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(6)

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

.....

.....

.....

.....

(Extra space) .....

.....

(1)

(Total 13 marks)

17 (a) Propanoic acid can be made from propan-1-ol by oxidation using acidified potassium dichromate(VI). Propanal is formed as an intermediate during this oxidation.

(i) State the colour of the chromium species after the potassium dichromate(VI) has reacted.

.....

(1)

(ii) Describe the experimental conditions and the practical method used to ensure that the acid is obtained in a high yield. Draw a diagram of the assembled apparatus you would use.

Conditions .....

.....

Apparatus

(4)

(iii) Describe the different experimental conditions necessary to produce propanal in high yield rather than propanoic acid.

.....

.....

(2)

(b) Propan-1-ol is a volatile, flammable liquid.
Give **one** safety precaution that should be used during the reaction to minimise this hazard.

.....

(1)

(c) A student followed the progress of the oxidation of propan-1-ol to propanoic acid by extracting the organic compounds from one sample of reaction mixture.

(i) Give a chemical reagent which would enable the student to confirm the presence of propanal in the extracted compounds.
State what you would observe when propanal reacts with this reagent.

Reagent .....

Observation .....

.....

(2)

(ii) Give a chemical reagent that would enable the student to confirm the presence of propanoic acid in the extracted compounds.
State what you would observe when propanoic acid reacts with this reagent.

Reagent .....

Observation .....

.....

(2)

(d) Predict which **one** of the compounds, propan-1-ol, propanal and propanoic acid will have the highest boiling point. Explain your answer.

Prediction .....

Explanation .....

.....

.....

.....

.....

(3)
(Total 15 marks)

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

Observation with 1-chloropropane

.....

.....

Observation with ethanoyl chloride.

.....

.....

(Total 2 marks)

19 Synthesis gas is a mixture of carbon monoxide and hydrogen. Methanol can be manufactured from synthesis gas in a reversible reaction as shown by the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H^{\ominus} = -91 \text{ kJ mol}^{-1}$$

(a) A sample of synthesis gas containing 0.240 mol of carbon monoxide and 0.380 mol of hydrogen was sealed together with a catalyst in a container of volume 1.50 dm^3.
When equilibrium was established at temperature T_1 the equilibrium mixture contained 0.170 mol of carbon monoxide.

Calculate the amount, in moles, of methanol and the amount, in moles, of hydrogen in the equilibrium mixture.

Methanol .....

Hydrogen .....

(2)

(b) A different sample of synthesis gas was allowed to reach equilibrium in a similar container of volume 1.50 dm^3 at temperature T_1

At equilibrium, the mixture contained 0.210 mol of carbon monoxide, 0.275 mol of hydrogen and 0.0820 mol of methanol.

(i) Write an expression for the equilibrium constant K_c for this reaction.

.....

.....

(1)

(ii) Calculate a value for K_c for the reaction at temperature T_1 and state its units.

Calculation ….....

.....

.....

.....

.....

Units .....

.....

(4)

(iii) State the effect, if any, on the value of K_c of adding more hydrogen to the equilibrium mixture.

.....

(1)

(c) The temperature of the mixture in part (b) was changed to T_2 and the mixture was left to reach a new equilibrium position. At this new temperature the equilibrium concentration of methanol had increased.

Deduce which of T_1 or T_2 is the higher temperature and explain your answer.

Higher temperature .....

Explanation .....

.....

.....

(3)

(d) The following reaction has been suggested as an alternative method for the production of methanol.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The hydrogen used in this method is obtained from the electrolysis of water.

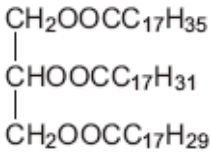
Suggest **one** possible environmental disadvantage of the production of hydrogen by electrolysis.

.....

.....

(1)

(e) One industrial use of methanol is in the production of biodiesel from vegetable oils such as



Give the formula of **one** compound in biodiesel that is formed by the reaction of methanol with the vegetable oil shown above.

.....

(1)

(Total 13 marks)

20 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.

.....

.....

.....

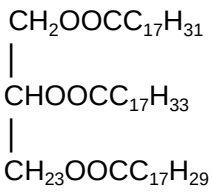
.....

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

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

.....

.....

.....

.....

.....

.....

.....

.....

(4)
(Total 19 marks)

21 Describe briefly how you could measure the melting point of aspirin.

.....

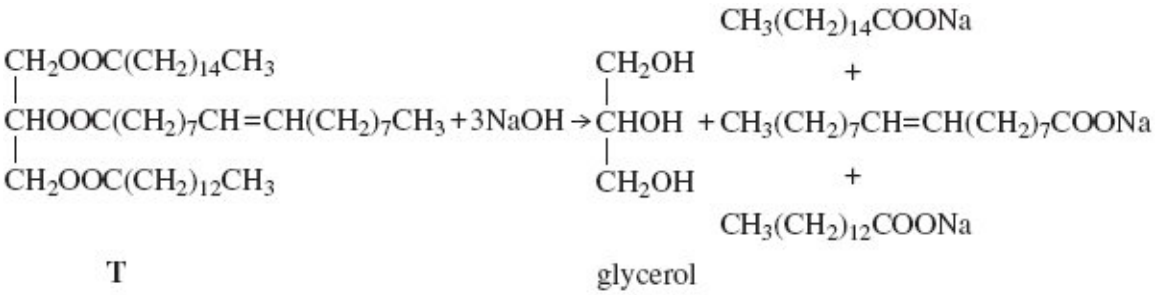
.....

.....

.....

(Total 2 marks)

22 The triester, **T**, shown below is found in palm oil. When **T** is heated with an excess of sodium hydroxide solution, the alcohol glycerol is formed together with a mixture of three other products as shown in the following equation.



T glycerol

(a) (i) Give the IUPAC name for glycerol.

.....

(1)

(ii) Give a use for the mixture of sodium salts formed in this reaction.

.....

(1)

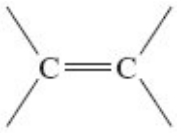
(b) When **T** is heated with an excess of methanol, glycerol is formed together with a mixture of methyl esters.

(i) Give a use for this mixture of methyl esters.

.....

(1)

(ii) One of the methyl esters in the mixture has the IUPAC name methyl (*Z*)-octadec-9-enoate. Draw **two** hydrogen atoms on the diagram below to illustrate the meaning of the letter *Z* in the name of this ester.



(1)

(iii) One of the other methyl esters in the mixture has the formula $CH_3(CH_2)_{12}COOCH_3$
Write an equation for the complete combustion of one molecule of this ester.

.....

(1)
(Total 5 marks)

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

Name the amide formed.

(6)

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

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

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

Equations and mechanisms are **not** required.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

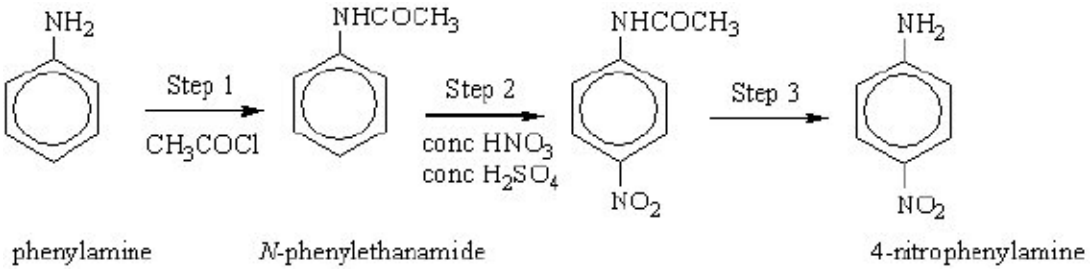
.....

.....

(6)
(Total 12 marks)

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

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



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

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

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

(ii) In a process where 10.0 kg of phenylamine are used, the yield of *N*-phenylethanamide obtained is 5.38 kg.

Calculate the percentage yield of *N*-phenylethanamide.

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

(7)

(b) Name and outline a mechanism for the reaction in Step 1.

(5)

(c) The mechanism of Step 2 involves attack by an electrophile. Write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

(4)

(Total 16 marks)

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

.....

(1)

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

Name of mechanism .....

Mechanism

(5)

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

(1)

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

.....

.....

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

.....

.....

(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.

.....

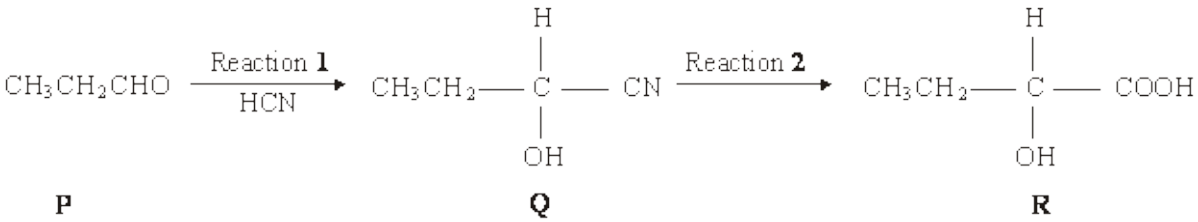
.....

.....

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

(3)
(Total 12 marks)

26 Consider the sequence of reactions below.



P **Q** **R**

(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)

27 (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)

28 (a) Compound **A**, $HCOOCH_2CH_2CH_3$, is an ester. Name this ester and write an equation for its reaction with aqueous sodium hydroxide.

Name ……

Equation .....

(2)

(b) The initial rate of reaction between ester **A** and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm^{-3}	Initial concentration of **A** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

*Order with respect to **A*** .....

Order with respect to NaOH .....

Initial rate in Experiment 4 .....

.....

(3)

(c) In a further experiment at a different temperature, the initial rate of reaction was found to be 9.0×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **A** was 0.020 mol dm^{-3} and the initial concentration of NaOH was 2.00 mol dm^{-3}.
Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

(i) Write a rate equation for the reaction under these new conditions.

.....

(ii) Calculate a value for the rate constant under these new conditions and state its units.

Calculation .....

.....

.....

Units .....

(iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

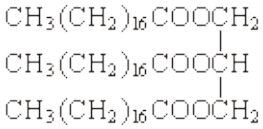
.....

.....

.....

(6)

(d) A naturally-occurring triester, shown below, was heated under reflux with an excess of aqueous sodium hydroxide and the mixture produced was then distilled. One of the products distilled off and the other was left in the distillation flask.



(i) Draw the structure of the product distilled off and give its name.

Structure

Name .....

(ii) Give the formula of the product left in the distillation flask and give a use for it.

Formula .....

Use .....

(4)
(Total 15 marks)

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

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

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

(7)

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

Reaction 1

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

Reaction 2

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

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

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

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

(8)

(Total 15 marks)

30 Which one of the following is **not** a correct general formula for the non-cyclic compounds listed?

A alcohols $C_nH_{2n+2}O$

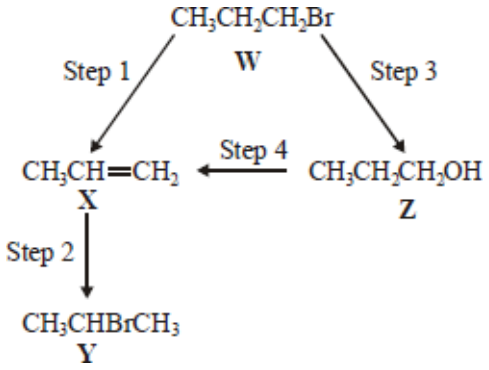
B aldehydes $C_nH_{2n+1}O$

C esters $C_nH_{2n}O_2$

C primary amines $C_nH_{2n+3}N$

(Total 1 mark)

31 For this question refer to the reaction scheme below.



Which one of the following statements is **not** correct?

A Reaction of **W** with sodium cyanide followed by hydrolysis of the resulting product gives propanoic acid.

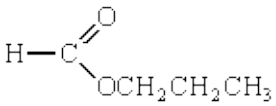
B Mild oxidation of **Z** produces a compound that reacts with Tollens' reagent, forming a silver mirror.

C **Z** reacts with ethanoic acid to produce the ester propyl ethanoate.

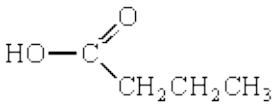
C **W** undergoes addition polymerisation to form poly(propene).

(Total 1 mark)

32 (a) Consider the following pair of isomers.



C



D

(i) Name compound **C**.

.....

(ii) Identify a reagent which could be used in a test-tube reaction to distinguish between **C** and **D**. In each case, state what you would observe.

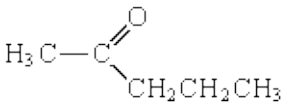
Reagent .....

*Observation with **C*** .....

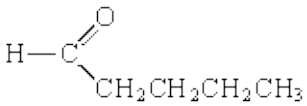
*Observation with **D***.....

(4)

(b) Consider the following pair of isomers.



E



F

(i) Name compound **E**.

.....

(ii) Identify a reagent which could be used in a test-tube reaction to distinguish between **E** and **F**. In each case, state what you would observe.

Reagent .....

*Observation with **E*** .....

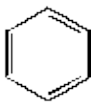
*Observation with **F***.....

(4)

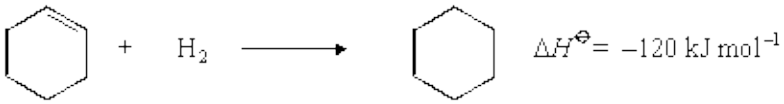
(c) Draw the structure of the chain isomer of **F** which shows optical isomerism.

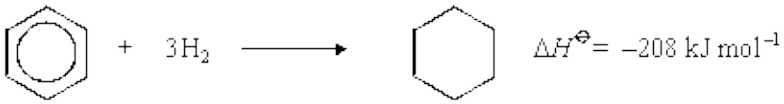
(1)
(Total 9 marks)

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



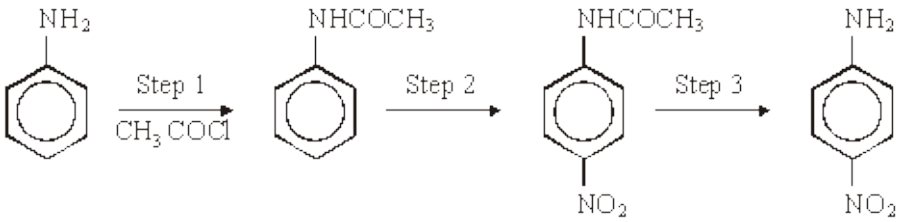
Give a reason for this difference in stability.





(4)

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



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

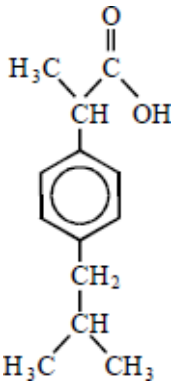
(ii) Name and outline a mechanism for the reaction in Step 1 and name the organic product of Step 1.

(iii) The mechanism of Step 2 involves attack by an electrophile. Give the reagents used in this step and write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

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

(17)
(Total 21 marks)

34 Ibuprofen is a drug used as an alternative to aspirin for the relief of pain, fever and inflammation. The structure of ibuprofen is shown below.



Which one of the following statements is **not** correct?

A It has optical isomers.

B It liberates carbon dioxide with sodium carbonate solution.

D It undergoes esterification with ethanol.

D It undergoes oxidation with acidified potassium dichromate(VI).

(Total 1 mark)

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

Mechanism

Name of product .....

(5)

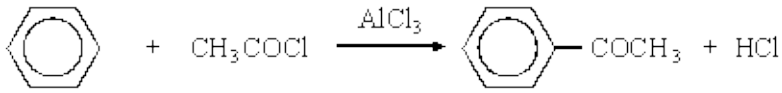
(b) Outline a mechanism for the reaction of CH_3OH with CH_3CH_2COCl and name the organic product.

Mechanism

Name of organic product .....

(5)

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



(i) Give the formula of the reactive intermediate.

.....

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

(4)
(Total 14 marks)

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

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

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

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

(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.

(9)

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

$CH_3COCl + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + HCl$

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

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

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

(4)
(Total 13 marks)

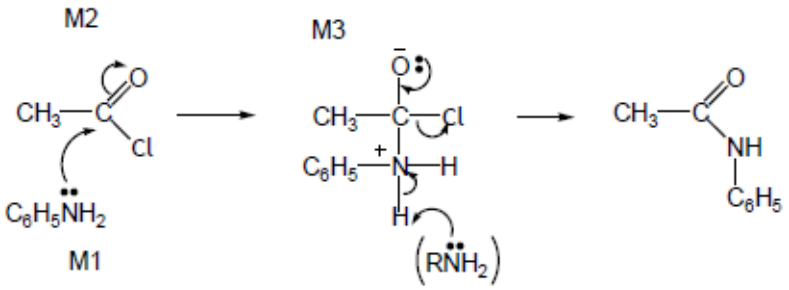
1 B

[1]

2 (a) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

1



M4 for 3 arrows and lp

Allow C_6H_5 or benzene ring

Allow attack by :$NH_2C_6H_5$

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

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

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

4

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

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

1

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

Yield lower if warm / solubility higher if warm

1

The crystals were compressed in the funnel:

Air passes through the sample not just round it

Allow better drying but not water squeezed out

1

A little cold water was poured through the crystals:

To wash away soluble impurities

1

(c) Water

Do not allow unreacted reagents

1

Press the sample of crystals between filter papers

Allow give the sample time to dry in air

1

(d) M_r product = 135.0

1

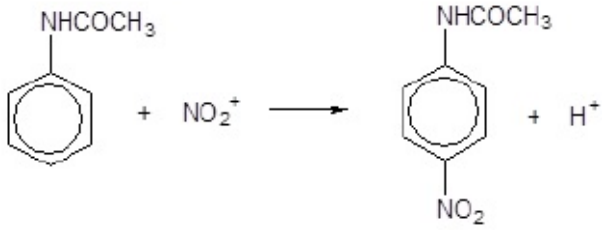
Expected mass = $5.05 \times \frac{135.0}{93.0} = 7.33$ g

1

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

Answer must be given to this precision

(e)



OR

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

1

(f) Electrophilic substitution

1

(g) Hydrolysis

1

(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

3

(a) (i) $(CH_3)_2CHOH + (CH_3CO)_2O \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$

Allow *$CH_3CO_2CH(CH_3)_2$ and CH_3CO_2H*

Ignore $(CH_3)_2$ −C in equation

1

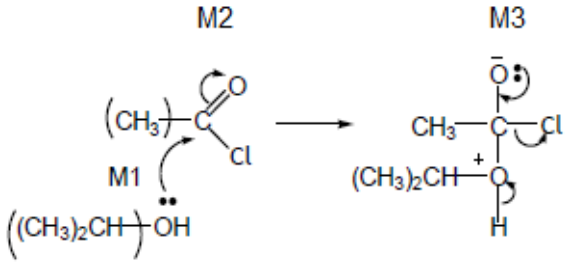
(1)-methylethyl ethanoate OR

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 δ+ on C=O loses M2*
- *If Cl lost with C=O breaking, max1 for M1*

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

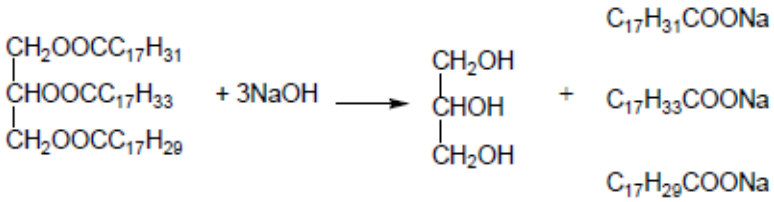
Penalise $(CH_3)_2$ −C in M3

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)



Penalise covalent Na e.g. -O-Na

LHS 1
RHS 1

(ii) $C_{17}H_{33}COOCH_3$

Allow $C_{19}H_{36}O_2$

1

[9]

4 (a) (i) M_r N−phenylethanamide = 135.0

1

Theoretical yield = 135.0 × 2 (1.15 / 284.1) = 1.09 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

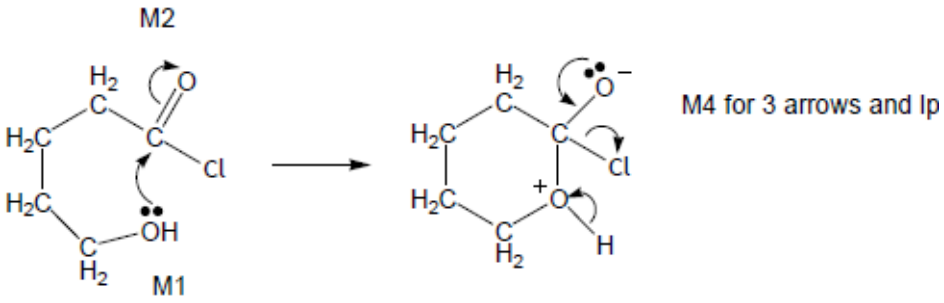
[15]

5 (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 <u>with charges</u> 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

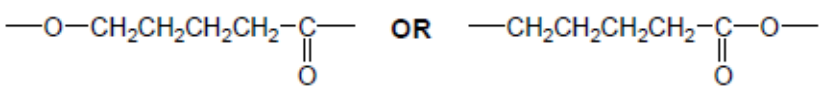
If values not specified as a or b then assume first is a.

1

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

1

(ii)

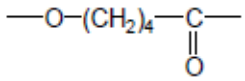


Must have trailing bonds, but ignore n.

1

OR –$OCH_2CH_2CH_2CH_2CO$– **OR** –$CH_2CH_2CH_2CH_2COO$–

Allow



but not - C_4H_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)

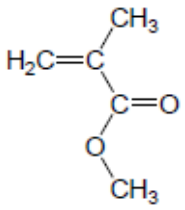
Ignore details of splitting.

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 $H_2C=C(CH_3)COOCH_3$

All $C_5H_8O_2$ L to P must have C=C.

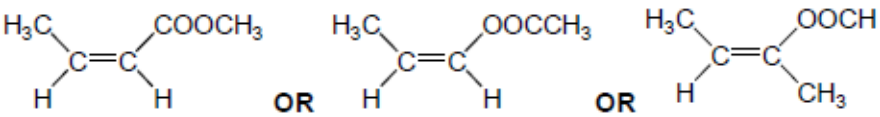
Allow CH_3–.

Allow $-CO_2CH_3$ etc.

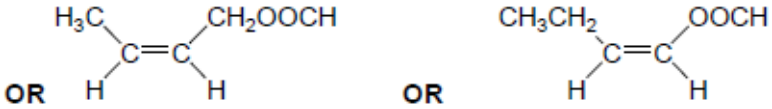
Allow $CH_2C(CH_3)COOCH_3$.

1

M
ester



$CH_3CH=CHCOOCH_3$ $CH_3CH=CHOOCCH_3$ $CH_3CH=C(CH_3)OOCH$



$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$

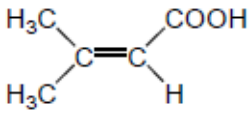
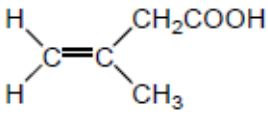
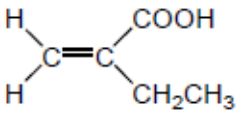
Allow either E–Z isomer.

Allow CH_3– or C_2H_5– but not CH_2CH_3–.

Allow $CH_3CHCHCOOCH_3$ etc.

1

N

acid  **OR**  **OR** 

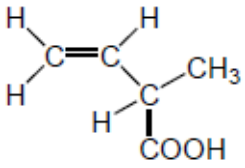
$(CH_3)_2C=CHCOOH$ $H_2C=C(CH_3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$

Allow CH_3– or C_2H_5– but not CH_2CH_3–.

Allow $-CO_2H$.

Not cyclic isomers.

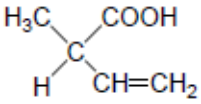
Not the optically active isomer.

 which is P anyway

Allow $(CH_3)_2CCHCOOH$ etc.

1

P

acid 

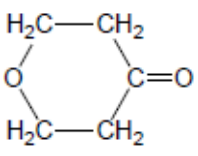
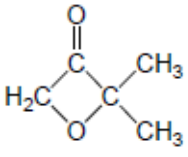
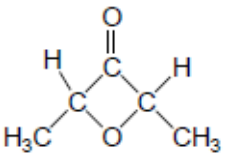
Allow $-CO_2H$.

$CH_3CH(COOH)CH=CH_2$

Allow $CH_3CH(CO_2H)CHCH_2$ or $CH_3CH(CO_2H)C_2H_3$.

1

Q

 **OR**  **OR** 

Not cyclic esters.

1

[19]

6 Identification of acid by suitable method eg named indicator, named carbonate, specified reactive metal

Ignore any reference to the smell of the ester.

1

with expected results

Do not allow the use of any instrumental method eg i.r. or n.m.r.; must be a <u>chemical</u> test.

1

Identification of alcohol by suitable method eg oxidation by acidified potassium dichromate(VI)

1

with expected results

1

[4]

7

(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]

8

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]

9 (a) (i) $\underline{3}CH_3OH$

Not molecular formula

1

$HOCH_2CH(OH)CH_2OH$

1

(ii) $\rightarrow \quad 19CO_2 \quad + \quad 19H_2O$

Or doubled

1

$C_{17}H_{35}COOCH_3 + 27½$ or $55/2\ O_2$

Consequential on correct right-hand side

1

(b) (i) A 0.7

1

Ethanol 6.4

1

Water 3.6

1

(ii) No effect

If wrong, CE= 0

1

Equal moles on each side of equation ***OR*** V cancels

Ignore moles of gas

1

(iii) M1 $K_c = \dfrac{[\text{DEM}][H_2O]^2}{[A][C_2H_5OH]^2}$

Must have all brackets but allow ( )

1

(iv) M2 $\frac{2.1 \times (3.4)^2}{0.85 \times (7.2)^2}$

If K_c wrong can only score M4 for units consequential to their K_c working in (b)(iv)

1

M3 0.55 (min 2dp)

1

M4 No units

1

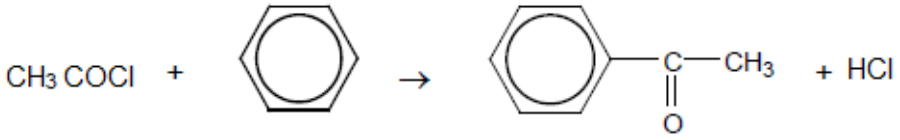
[13]

10 (a) (i) $CH_3COCl + C_6H_6 \rightarrow C_6H_5COCH_3 + HCl$

Not molecular formulae *Not allow $C_6H_5CH_3CO$*

1

OR



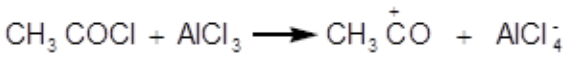
phenylethanone

Ignore number 1 in name but penalise other numbers

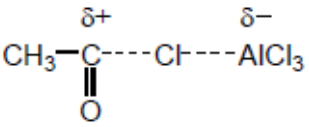
1

$AlCl_3$ can be scored in equation

1



Allow RHS as



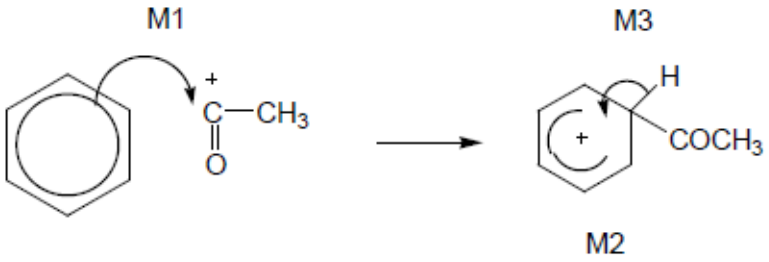
Allow + on C or O in equation but + must be on C in mechanism below

Ignore curly arrows in balanced equation even if wrong

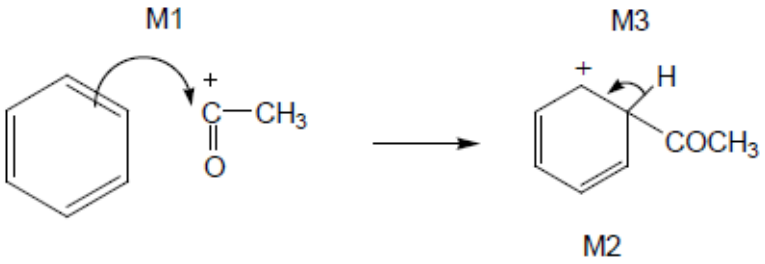
1

(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*

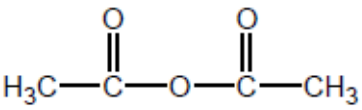
3

(b) Electron <u>pair donor</u> or lone <u>pair donor</u>

Allow donator

Allow lone pair used in description of (dative) bond formation

1



Allow $(CH_3CO)_2O$

1

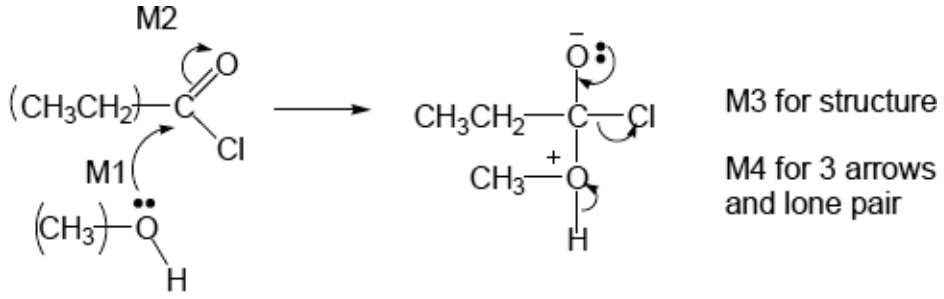
(acid) anhydride

Allow ethanoic anhydride but not any other anhydride

1

[11]

11 (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^+*

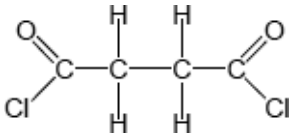
4

(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

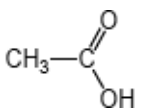
M3 reacts with OH^- or hydroxide ion

1

Not reacts with NaOH

1

(c) (i)



Allow CH_3COOH or CH_3CO_2H

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

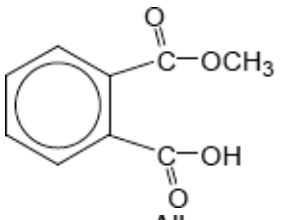
- less corrosive
- less vulnerable to hydrolysis
- less dangerous to use,
- less violent/exothermic/vigorous reaction OR more controllable rxn
- does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl
- less volatile

***NOT** COST*

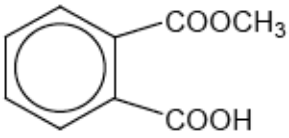
List principle beyond two answers

2

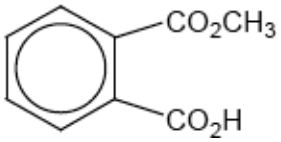
(d)



Allow



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]

12 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]

13 (a) $Mg + 2C_6H_4(OH)COOH \rightarrow (C_6H_4(OH)COO)_2Mg + H_2$

Accept multiples, including fractions.

1

(b) Gas syringe / inverted burette over water / measuring cylinder over water

Collection apparatus must show graduations or be clearly labelled (eg syringe, burette, measuring cylinder).

1

[2]

14 (a) $CH_3(CH_2)_{14}COOH$

Allow molecular formulae.

1

$CH_2OHCHOHCH_2OH$

Allow one mark only if formulae are swapped in position.

1

(b) Keeping the foodstuff dry

Allow an answer which refers to removal of water from the environment.

Do not allow dehydration / removal of water from the fat.

1

(c) They (antioxidants) react with free radicals

1

And they are used up in the reaction / do not remain behind after reaction

Lose one mark for any reference to 'catalysts can't slow down a reaction'.

1

(d) Mol of fat = (2.78 / 806 =) 3.45×10^{-3}

Mol of NaOH = 3.68×10^{-3} = mol of fatty acid

1

Mol of NaOH = 3.68×10^{-3}

Mol of fat hydrolysed = 1.23×10^{-3}

1

Mol of fat hydrolysed = (3.68×10^{-3} / 3 =) 1.23×10^{-3}

Mass of fat hydrolysed = 0.987 g

1

Percentage hydrolysed = 35.5 – 35.7

Percentage hydrolysed = 35.5 – 35.7

Do not penalise precision at any point.

Since there are a variety of approaches to this calculation, award four marks for a correct answer but it must be clear that there is some relevant working.

The answer alone gets M4 only.

Any incorrect use of the 3:1 ratio is CE – lose M3 and M4.

1

[9]

15 (a) Melting range would be
wide (>3 deg C) / not sharp

Allow melts over a range of temperatures.

1

below / before the true m.p.

Do not allow 'above or below'.

1

(b) Temperature on thermometer not the same as the sample

Allow sample heats up at a different / higher / lower rate than thermometer.

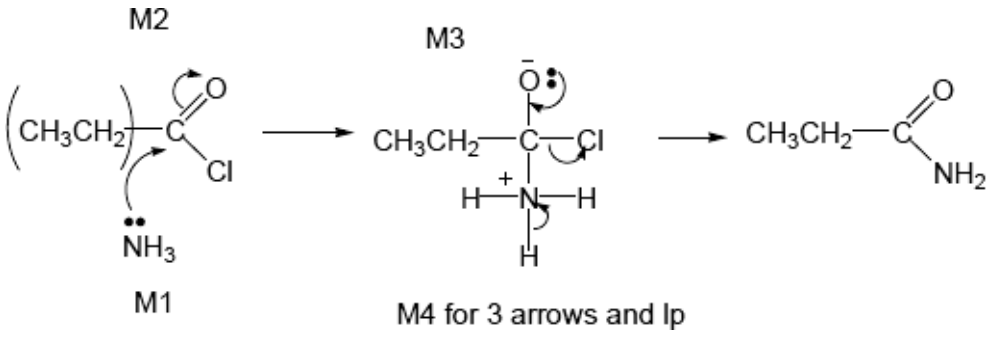
1

[3]

16 (a) (Nucleophilic) addition-elimination

- *Minus sign on NH_3 loses M1(but not M4 also)*
- *M2 not allowed independent of M1, but*

1



M4 for 3 arrows and lp

- *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***
- *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

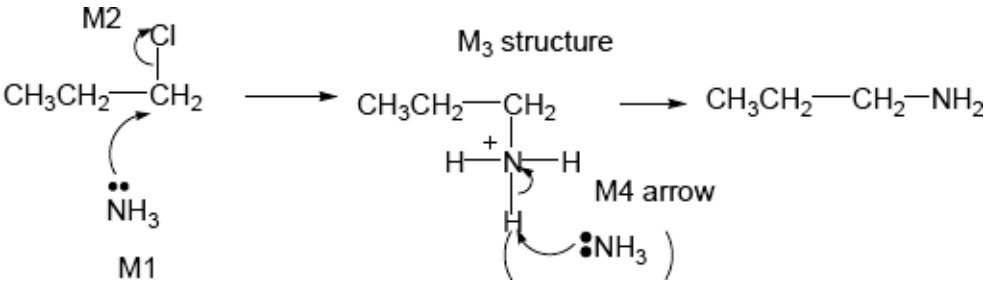
penalise propaneamide and N-propanamide

1

(b) Nucleophilic substitution

- *Minus sign on NH_3 loses M1 (not M4 also)*
- *+ rather than δ+ on C=O loses M2*

1



- *ALLOW SN1 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]

17 (a) (i) Green

Ignore shades of green.

1

(ii) Excess acidified potassium dichromate(VI)

1

Reflux (for some time)

1

In the diagram credit should be given for

- a vertical condenser

Lose M3 and M4 for a distillation apparatus.

1

- an apparatus which would clearly work

Do not allow this mark for a flask drawn on its own.

Penalise diagrams where the apparatus is sealed.

1

(iii) Distillation

1

Immediately (the reagents are mixed)

1

(b) Keep away from naked flames

Allow heat with water-bath or heating mantle.

If a list is given ignore eye protection, otherwise lose this mark.

1

(c) (i) Tollens' or Fehling's reagents

*Incorrect reagent(s) loses **both** marks.*

Accept mis-spellings if meaning is clear.

1

Silver mirror / red ppt. formed

Accept 'blue to red' but not 'red' alone.

1

(ii) Sodium carbonate (solution) / Group II metal

Allow indicator solutions with appropriate colours.

Accept any named carbonate or hydrogen carbonate.

1

Effervescence / evolves a gas

Accept 'fizzes'.

1

(d) Propanoic acid

If this mark is lost allow one mark if there is reference to stronger intermolecular forces in the named compound.

Lose M1 and M3.

1

Contains hydrogen bonding

1

Some comparison with other compounds explaining that the intermolecular forces are stronger in propanoic acid

1

[15]

18 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]

19 (a) mol CH_3OH = 0.07(0)

1

mol H_2 = 0.24(0)

1

(b) (i) $\frac{[CH_3OH]}{[CO][H_2]^2}$ or $\frac{(0.082/1.5)}{(0.210/1.5)(0.275/1.5)^2}$

allow ( ) but expression using formulae must have brackets
alternative expression using numbers must include volumes

1

(ii) **M1** divides by vol

Mark independently from (b)(i)
any AE is –1
if volume missed, can score only M3 and M4

1

M2 $\frac{(0.082/1.5)}{(0.210/1.5)(0.275/1.5)^2}$ $\left(= \frac{(0.05467)}{(0.14)(0.1833)^2}\right)$

mark is for correct insertion of correct numbers in correct Kc expression in b(ii)
If Kc expression wrong, can only score M1 & M4
If numbers rounded, allow M2 but check range for M3

1

M3 11.6 or 11.7

mark for answer
above 11.7 up to 12.2 scores 2 for M1 and M2
if vol missed, can score M3 for 5.16 (allow range 4.88 to 5.21)

1

M4 $mol^{-2}\ dm^6$

Units conseq to their Kc in (b)(ii)

1

(iii) no effect or no change or none

1

(c) **M1** T_1

if wrong - no further marks

1

M2 (forward) reaction is exothermic **OR** gives out heat

backward reaction is endothermic

only award M3 if M2 is correct

1

M3 shifts to RHS to replace lost heat

OR to increase the temperature

OR to oppose fall in temp

backward reaction takes in heat

OR to lower the temperature

not just to oppose the change

1

(d) fossil fuels used

OR

CO_2 H_2O produced/given off/formed which are greenhouse gases

OR

SO_2 produced/given off/formed which causes acid rain

OR

Carbon produced/given off/formed causes global dimming

not allow electricity is expensive
ignore just global warming
ignore energy or hazard discussion

1

(e) $C_{17}H_{35}COOCH_3$ **or** $C_{17}H_{31}COOCH_3$ or $C_{17}H_{29}COOCH_3$

OR

$CH_3OOCC_{17}H_{35}$ or $CH_3OOCC_{17}H_{31}$ or $CH_3OOCC_{17}H_{29}$

1

[13]

20 (a) **M1** $CH_3CH_2CH_2COOH$

not C_3H_7COOH

1

M2 CH_3CH_2OH or C_2H_5OH

1

M3 $CH_3CH_2CH_2COOCH_2CH_3 + H_2O$

allow $C_3H_7COOC_2H_5$

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** $CH_3CH_2CH_2CH_2OH$

1

not C_4H_9OH

M2 $(CH_3CO)_2O$

1

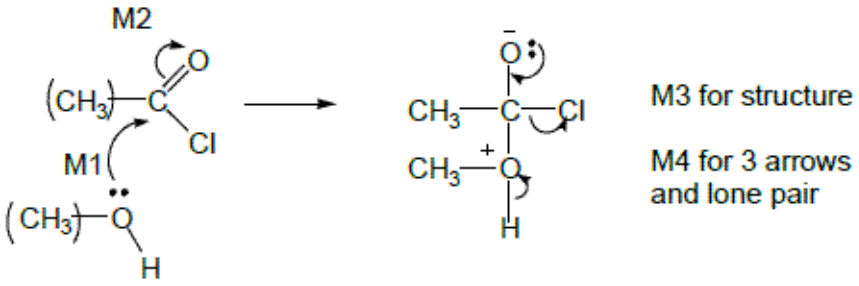
M3 → $CH_3COOCH_2CH_2CH_2CH_3 + CH_3COOH$

allow $CH_3COOC_4H_9$

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+

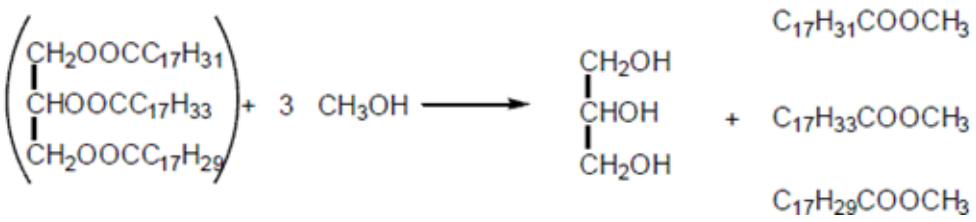
+C=O loses M2

only allow M4 after correct or v close M3

ignore Cl^- removing H^+

5

(d)



(1) (1) (1)

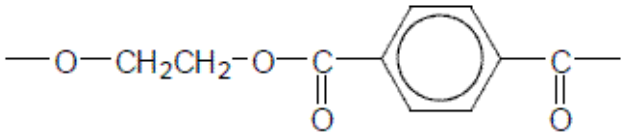
ignore errors in initial triester

First mark for $3CH_3OH$

Third mark for all three esters

3

(e) not $-C_2H_4-$



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 CO_2 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]

21 Sample in capillary / melting point tube

Accept alternative as long as small container used

1

Heat in melting point apparatus / heat <u>gently / slowly</u> near melting point

1

[2]

22 (a) (i) propan(e)-1,2,3-triol or 1,2,3- propan(e)triol

not propyl
ignore hyphen, commas

1

(ii) soaps

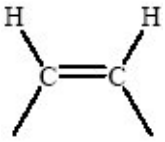
allow anionic surfactant
not cationic surfactant
not detergents, not shampoos

1

(b) (i) (bio)<u>diesel</u>

Allow fuel for <u>diesel</u> engines
not biofuel, not oils

1

(ii) 

ignore anything else attached except any more H atoms.

1

(iii) $CH_3(CH_2)_{12}COOCH_3 + 21½O_2 \rightarrow 15CO_2 + 15\ H_2O$

OR

$C_{15}H_{30}O_2$ or 43/2

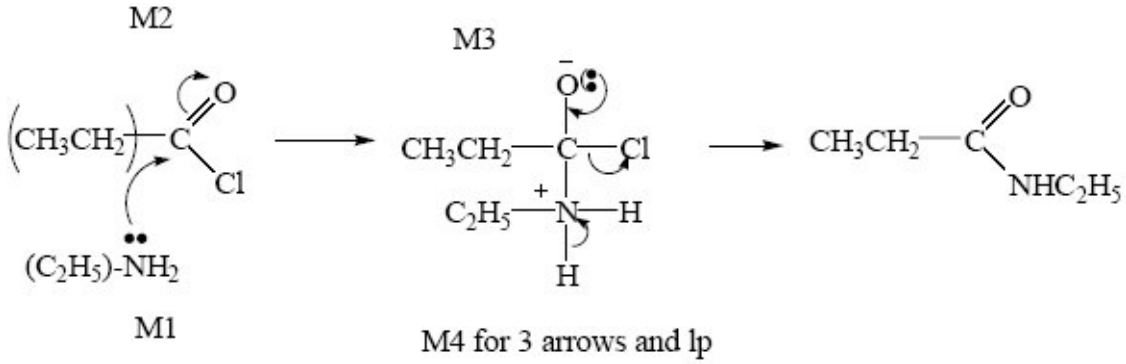
***not** allow equation doubled*

1

[5]

23 (a) (nucleophilic) addition-elimination

1



4

N-ethylpropanamide

minus on NH_2 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) CH_3CN 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 Cl_2
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 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH

not CN^- but mark on
NOT HCN or KCN + acid, and this loses condition mark
NOT $NaBH_4$
Sn/HCl (forms aldehyde!)
ignore conditions

1

[12]

24

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

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

1

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

1

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

1

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

1

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

1

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

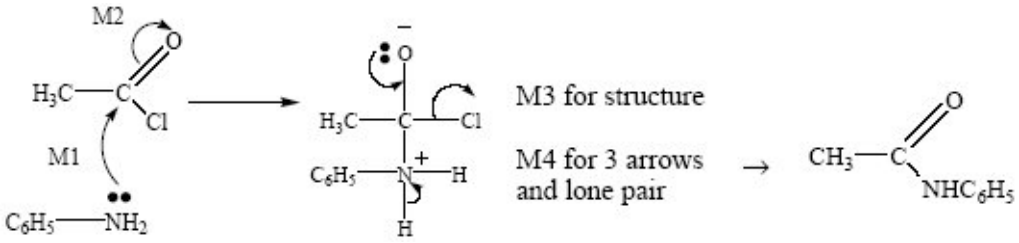
1

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

1

(b) (nucleophilic) addition-elimination

1

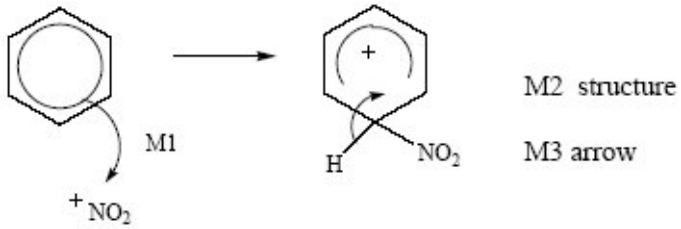


QWC (2)

4

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

1



3

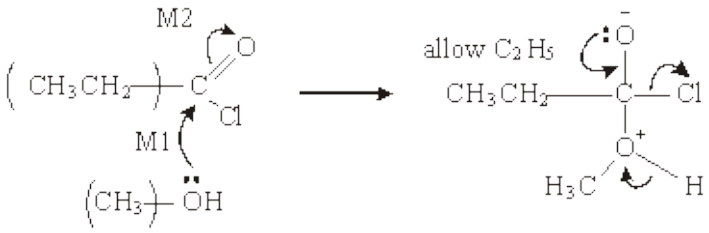
[16]

25 (a) $CH_3OH + CH_3CH_2COOH \rightarrow CH_3CH_2COOCH_3 + H_2O$

1

(b) (nucleophilic) addition–elimination NOT acylation

1



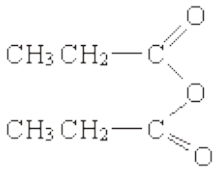
ignore use of Cl^- to remove H^+

M3 for structure

M4 for 3 arrows and lone pair

4

(c)



allow C_2H_5 and $–CO_2–$

allow $CH_3CH_2COOCOCH_2CH_3$

or *$(CH_3CH_2CO)_2O$*

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

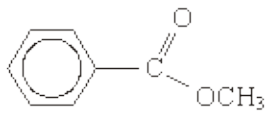
any one

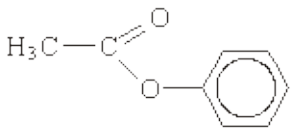
1

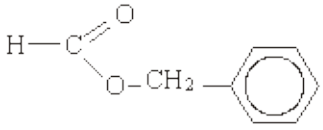
(e) (i) $C_8H_8O_2$

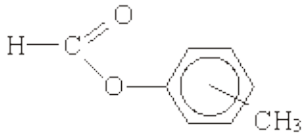
1

(ii) **any** two **from**









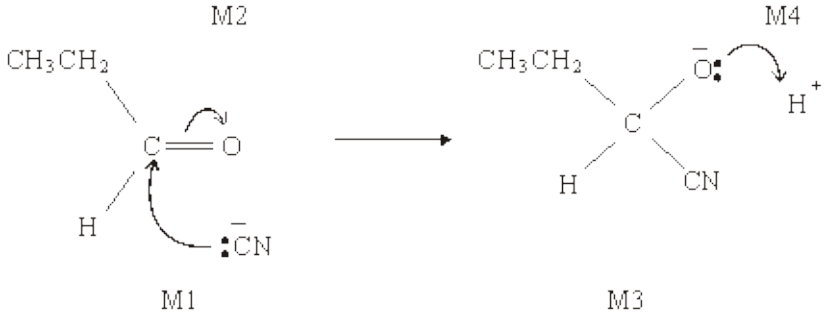
Allow –CO_2– allow C_6H_5

2

[12]

26 (a) nucleophilic addition

1

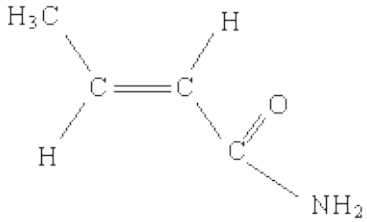


4

(b) (i) 2-hydroxybutanenitrile

1

(ii)

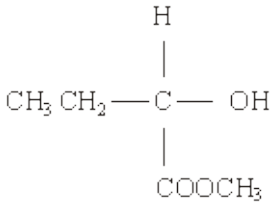


(allow 1 for amide even if not C_4H_7NO, i.e. $RCONH_2$)

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

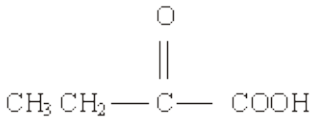
2

(c) (i)



1

(ii)



1

(iii) $CH_3CH=CHCOOH$

1

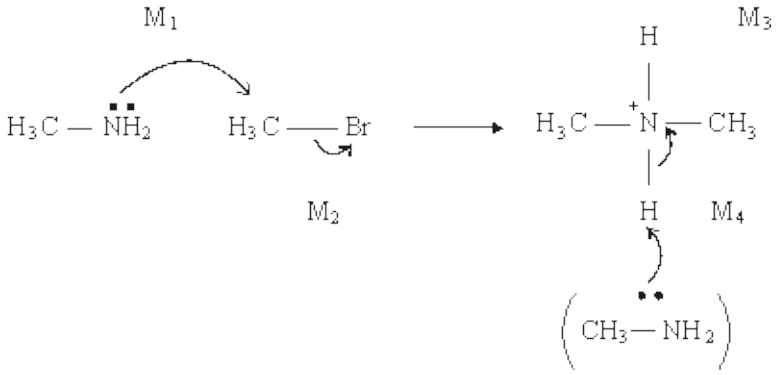
[11]

27 (a) dimethylamine

1

(b) nucleophilic substitution

1



4

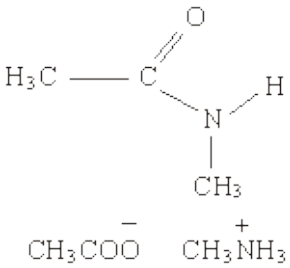
(c) quaternary ammonium salt

1

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

1

(d)



(allow CH_3COOH or $CH_3COO^-\ NH_4^+$)

2

[10]

28 (a) propyl methanoate;

$HCOOC_3H_7 + OH^- \rightarrow HCOO^- + C_3H_7OH$

1

OR

$HCOOC_3H_7 + NaOH \rightarrow HCOONa + C_3H_7OH$;

1

(b) order wrt A = 1;

1

order wrt NaOH = 1;

1

Initial rate in Exp 4 = 2.4×10^{-3};

1

(c) (i) r(ate) = k[A]

OR

r(ate) = $k[A][NaOH]^0$;

(penalise missing [ ] but mark on)
(penalise missing [ ] once per paper)
(if wrong order, allow only units mark conseq on their rate eqs)
(penalise k_a or k_w etc)

1

(ii) $k = \frac{9.0 \times 10^{-3}}{0.02}$;

1

= 0.45;

1

s^{-1};

1

(iii) (large) excess of OH^- or $[OH^-]$ is large/high;

1

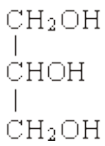
$[OH^-]$ is (effectively) constant

OR

[A] is the limiting factor *(Q of L mark)*

1

(d) (i)



1

propan(e)-1,2,3-triol

OR

1,2,3-propan(e)triol

OR

Glycerol;

1

(ii) $CH_3(CH_2)_{16}COONa$ or $C_{17}H_{35}COONa$ or $C_{18}H_{35}O_2Na$;

(ignore 3 in front of formula but not if indicating trimer)

1

(not just anion and penalise Na shown as covalently bonded) soap - allow with detergent but not detergent alone;

1

[15]

29 (a) *M1* $K_p = ({}_PY)^3.({}_PZ)^2/({}_PW)^2.({}_PX)$ *NB [ ] wrong*

1

M2 temperature

1

M3 increase

1

M4 particles have more energy or greater velocity/speed

1

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

1

M6 Reaction exothermic or converse

1

M7 Equilibrium moves in the left

1

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

1

Disadvantage; reaction vigorous/dangerous

(exothermic must be qualified)

or HCl(g) evolved/toxic
or CH_3COCl expensive

NB Allow converse answers
Do not allow reactions with other reagents e.g. water or ease of separation

1

(ii) $\Delta S = \Sigma S$ products – ΣS reactants

1

ΔS = (259 + 187) – (201 + 161)

1

ΔS = 84 (JK^{-1} mol^{-1}) *(Ignore units)*

*Allow – 84 to score **(1)** mark*

1

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

1

= – 21.6 – 298 × 84/1000

= – 46.6 kJ mol^{-1} or – 46 600 J mol^{-1}

1

*Allow **(2)** for – 46.6 without units*

(Mark ΔG consequentially to incorrect ⊿S)

(e.g. ⊿S = –84 gives ⊿G = +3.4 kJ mol^{-1})

1

[15]

30 B

[1]

31 A

[1]

32 (a) (i) propyl methanoate **(1)**

not propanyl

- *A wrong reagent or no reagent scores zero*
- *An incomplete reagent such as silver nitrate for Tollens, or potassium dichromate loses the reagent mark, but can get both observation marks*
- *penalise observations which just say colour change occurs or only state starting colour*

(ii) *Reagent*: $NaHCO_3$ **(1)**
*Observation with **C***: no reaction **(1)**
*Observation with **D***: effervescence **(1)**
*for **C** and **D** NOT Tollens*

Test	an identified (hydrogen) carbonate	acidified $K_2Cr_2O_7$	acidified $KMnO_4$	correct metal	UI or stated indicator	PCl_5
Observation with C	no reaction	goes green	goes colourless	no reaction	no change	no reaction
observation with D	bubbles or CO_2	no change	no change	bubbles or H_2	red or correct colour pH 3 – 6.9	(misty) fumes

4

(b) (i) *Reagent*: pentan-2-one **(1)**
or 2-pentanone
but not pent-2-one or pentyl

(ii) *Reagent*: Tollen's or Fehling's **(1)**

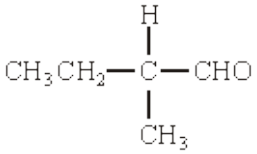
*Observation with **E***: no reaction **(1)**

*Observation with **F***: silver mirror or red ppt **(1)**

for **E** and **F**

Test	Tollens	Fehlings or Benedicts	iodoform or I_2/NaOH	acidified $K_2Cr_2O_7$	Schiff's
observation with E	no reaction	no reaction	yellow (ppt)	no change	no reaction
observation with F	silver or mirror or grey or ppt	red or ppt not red solution	no reaction	goes green	goes pink

4

(c)  **(1)**

must be aldehyde. Allow C_2H_5 for CH_3CH_2 otherwise this is the only answer

1

[9]

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

∴ (expect triene to evole) 360 kJ mol^{-1} **(1)** or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

*QofL: benzene lower in energy / <u>more</u> (stated) stable **(1)***
Not award if mentions energy required for bond breaking
*due to <u>delocalisation</u> **(1)** or explained*

4

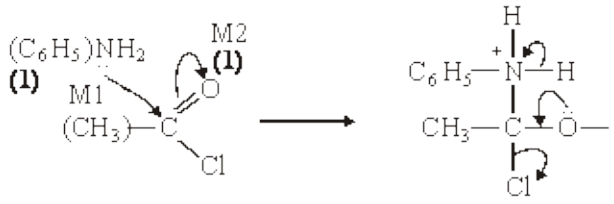
(b) (i) phenylamine weaker **(1)**

if wrong no marks

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

3

(ii) addition – elimination **(1)**



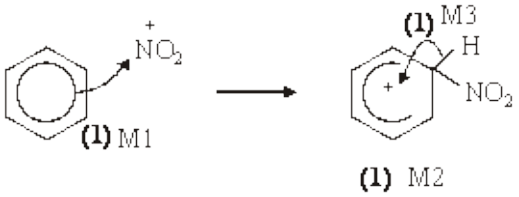
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)**
conc H_2SO_4 **(1)**

$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$ **(1)**



6

(iv) peptide / amide **(1)**

NaOH (aq) **(1)**

HCl conc or dil or neither

H_2SO_4 dil NOT conc

NOT just H_2O

2

Notes

(a)
- 360 or 3 × 120 or in words **(1)**;
- 152 NOT 150 **(1)**; (152 can get first two marks)
- **Q of L** benzene more stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene **(1)**;
- delocalisation or explained **(1)**

(b) (ii) or N-phenylacetamide or acetanilide
mechanism: if shown as substitution can only gain M1
if CH_3CO+ formed can only gain M1
lose M4 if Cl^- removes H^+
be lenient with structures for M1 and M2 but must be correct for M3
C=O alone loses M2

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

allow $HNO_3 + H_2SO_4 \rightarrow NO^{2+} + HSO_4^- + H_2O$
ignore side chain in mechanism even if wrong
arrow for M1 must come from niside hexagon
arrow to NO_2^+ must go to N but be lenient over position of +
+ must not be too near “tetrahedral” Carbon
horseshoe from carbons 2-6 but don’t be too harsh

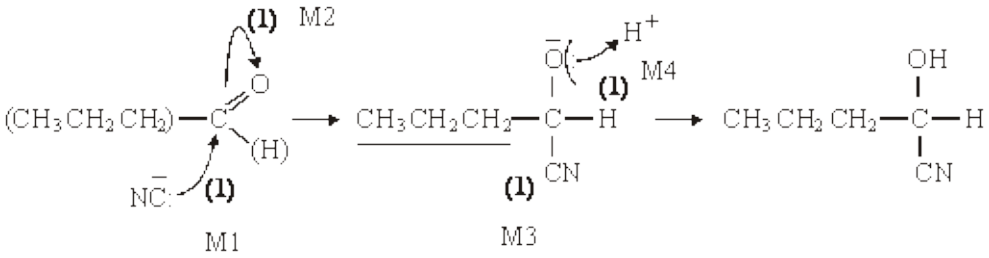
(iv) reagent allow NaOH
HCl conc or dil or neither
H_2SO_4 dil or neither but not conc
not just H_2O

[21]

34 D

[1]

35 (a) *Mechanism*



Allow C_3H_7 if structure shown elsewhere

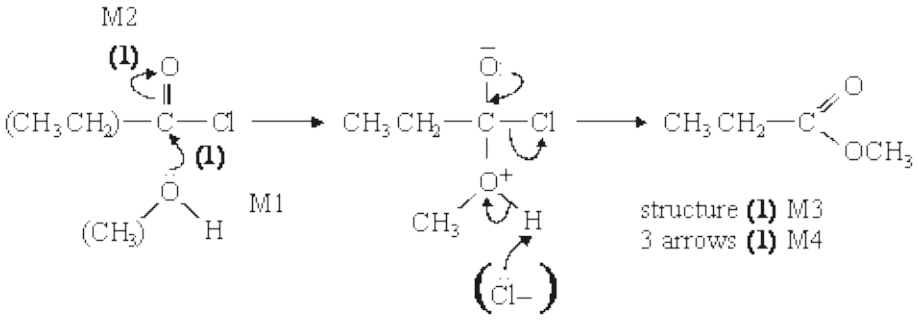
penalise HCN splitting if wrong

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

or 1-cyanobutan-1-ol

5

(b) *Mechanism*

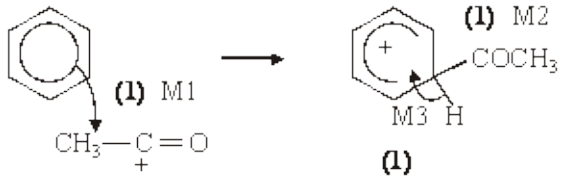


Name of organic product: methylpropanoate **(1)**

5

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

(ii)



4

Notes

(abc) extra curly arrows are penalised

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

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

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

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

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

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

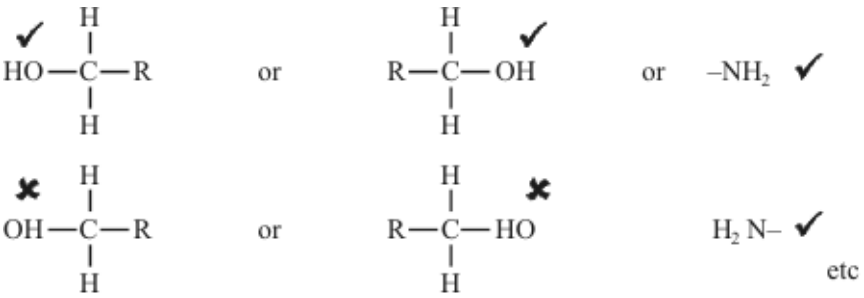
[14]

Organic points

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

(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

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

36 (a) (i) Moles NaOH = mv/1000 = 1.50 × 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 = [Ester] [Water]/[Acid] [Alcohol] **(1)**

Allow if used correctly

= $(0.091)^2/0.109 \times 0.019$ = 3.7 to 4.9 **(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 CH_3COOH 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]