WJEC EDUQAS A-LEVEL CHEMISTRY · COMPONENT 2

CHEMISTRY



EXAM QUESTION PACK

OA2.3 CARBOXYLIC ACIDS AND DERIVATIVES

SCORE	PERCENTAGE
/105	%

STEMUP

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1. State the reagent(s) used and the colour change seen when a primary alcohol is oxidised to give a carboxylic acid.

[2]

Reagent(s).....

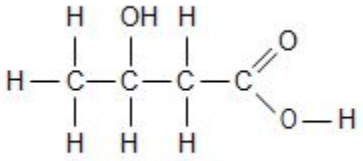
Colour change from. . . . . *to* . . . . . .

(Total 2)

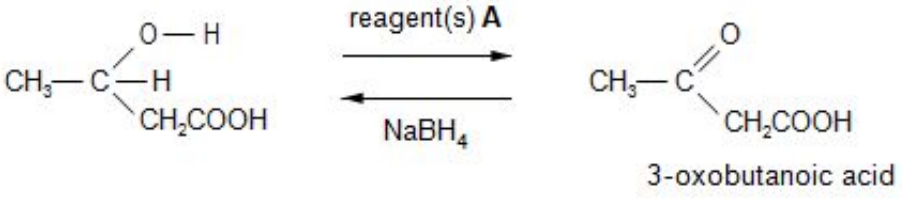
2. 3-Hydroxybutanoic acid is a white solid that can react as a carboxylic acid and an alcohol.

(a) Indicate the position of any chiral centre in the formula of 3-hydroxybutanoic acid by use of an asterisk (*).

[1]



(b) The acid can be oxidised to an oxoacid by using reagent(s) **A**. This oxoacid can then be reduced back to the hydroxyacid by sodium tetrahydridoborate(III), $NaBH_4$.



(i) State the name(s) of reagent(s) **A**.

[1]

(ii) The reduction of the oxoacid gives 3-hydroxybutanoic acid, which is present as a racemic mixture.

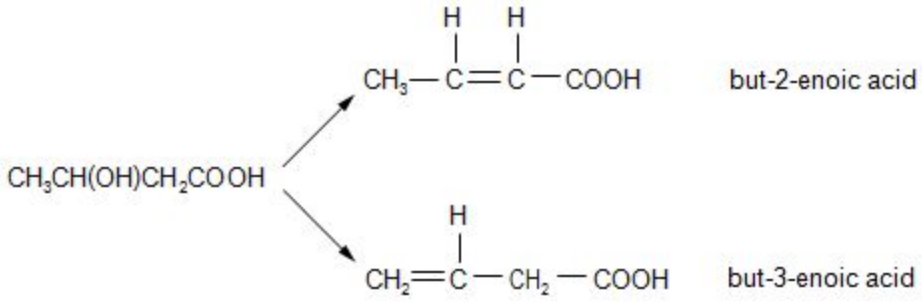
I. State what is meant by the term ***racemic mixture***.

[1]

II. State the effect (if any) that a racemic mixture has on the plane of polarised light.

[1]

(c) 3-Hydroxybutanoic acid readily undergoes an elimination reaction to form a mixture of unsaturated acids.



(i) State which of these unsaturated acids exists as *E*-*Z* isomers, giving a reason for your answer.

[1]

(ii) A scientist reported that the yield of the products was but-2-enoic acid 89%, but-3-enoic acid 4% together with unreacted 3-hydroxybutanoic acid 7%.

State any additional information that another scientist would have to know so that the experiment could be repeated to confirm these yields.

[2]

1. _____

2. _____

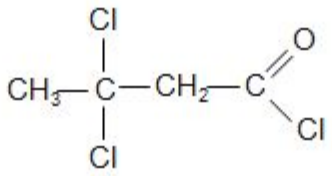
(d) Both 3-hydroxybutanoic acid and 3-oxobutanoic acid will undergo the triiodomethane (iodoform) reaction. State the reagent(s) used for this reaction and the observation made.

[2]

Reagent(s). . . . . .

Observation. . . . . .

(e) 3-Oxobutanoic acid reacts with phosphorus(V) chloride to give 3,3-dichlorobutanoyl chloride.



Describe the NMR spectrum of this chloro-compound.

In your answer you should include the following points, **giving an explanation for each**.

• the number of peaks (and their approximate position in ppm)

• the relative peak areas

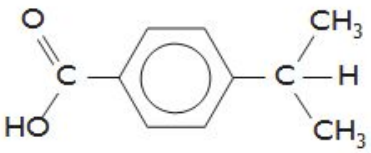
• any splitting pattern3

[3] QWC [1]

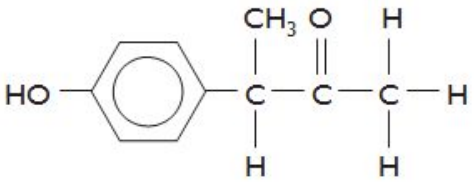
(Total 13)

3.

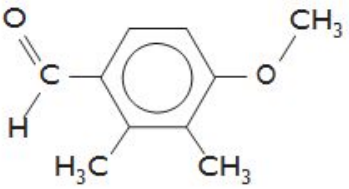
This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



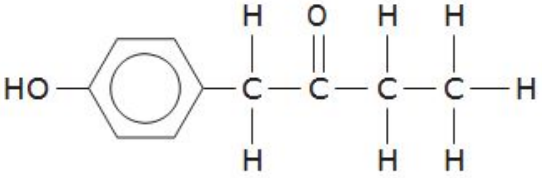
compound **W**



compound **x**



compound **y**



compound **Z**

(a) Draw an **ester** which is an isomer of the compounds above.

[1]

(b) Only one of the compounds shown can exhibit optical isomerism

(i) Identify which compound can exhibit optical isomerism.

[1]

(ii) Indicate the chiral centre in this molecule by labelling it with an asterisk (*).

[1]

(iii) State how the two enantiomers of this compound can be distinguished.

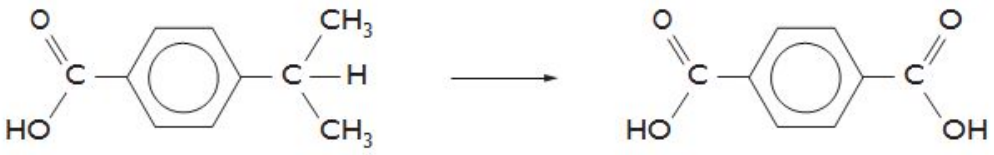
[1]

(c) The four compounds **W**, **x**, **y** and **Z** were tested using a series of reagents. For each of the tests listed below, describe what would be expected to be observed in a positive test. Indicate which compounds would be expected to give a positive result. [6]

All the tests listed will give positive results with at least one compound.

Reagent(s)	*Observation if the test is positive*	*Compounds that would give a positive result*
I_2/NaOH(aq)	.....	.....
Na_2CO_3(aq)	.....	.....
$FeCl_3$(aq)	.....	.....

(d) Compound **W** can be oxidised to produce benzene-1,4-dioic acid *(terephthalic acid)*. This reaction can be undertaken in the same way as the oxidation of methylbenzene to form benzenecarboxylic acid.



compound **W**

benzene-1,4-dioic acid
(terephthalic acid)

(i) Give the reagent(s) and condition(s) required for this oxidation reacti

[2]

(ii) Almost all the benzene-1,4-dioic acid produced worldwide is used in the production of condensation polymers

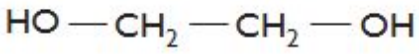
I. Give **two** differences between condensation polymerisation and addition polymerisation.

[2]

II. Draw the repeat unit for the polymer formed between benzene-1,4-dioic acid and ethane-1,2-diol. [1]

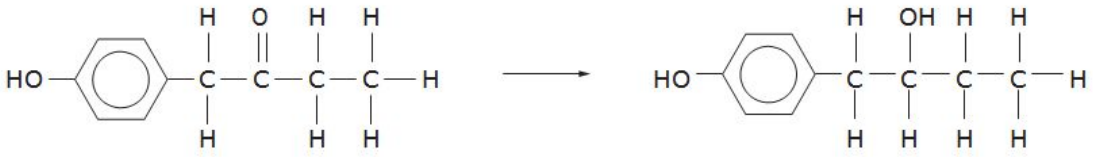


benzene-1,4-dioic acid
(terephthalic acid)



ethane-1,2-diol

(e) Compound **Z** may be converted into a secondary alcohol as shown below.



compound **Z** compound **V**

(i) Give a suitable reagent for this process and classify the reaction that occurs. [2]

Reagent .....

Classification of reaction .....

(ii) Compound **V** will react with ethanoyl chloride.Give the structure of a carbon-containing product of this reaction.

[1]

(iii) Compound **V** is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.Give the structure of the carbon-containing species present in the resulting solution.

[1]

(Total 19)

4. Mauveine is a purple dye that was developed by Perkin in 1856 and was one of the first organic compounds to be synthesised on a large scale. He is credited with launching the synthetic chemical industry.

(a) Give the name for the part of a molecule that causes it to be coloured.

[1]

(b) The dye mauveine often contains a mixture of impurities. Iwan and Georgia wanted to confirm that a sample of the dye was impure.

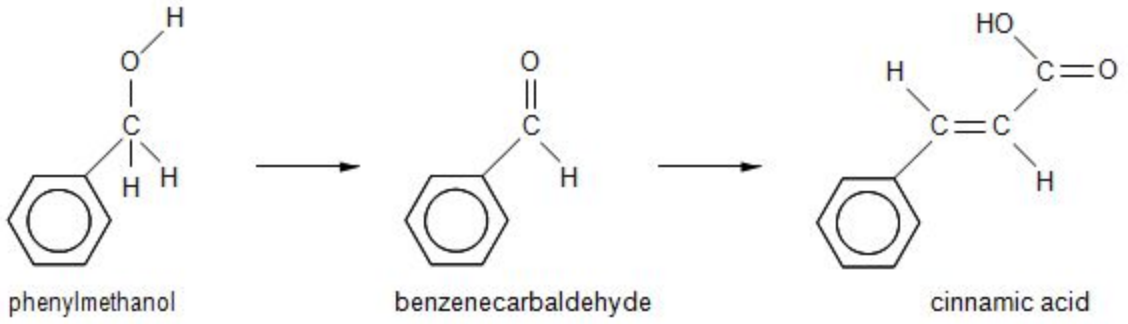
(i) Iwan used the melting temperature of the sample to confirm that the sample was impure. Give **one** way that the melting temperature would show this.

[1]

(ii) Georgia used gas chromatography to confirm that the sample was impure. State what information she obtained using this method that Iwan could not obtain from the melting temperature.

[2]

(c) Another compound synthesised by Perkin was cinnamic acid. Cinnamic acid can be produced in two steps from phenylmethanol as shown below.



phenylmethanol benzenecarbaldehyde cinnamic acid

(i) Give the reagent(s) and condition(s) required to obtain a sample of benzenecarbaldehyde from phenylmethanol.

[2]

Reagent(s) . . . . . .

Condition(s) . . . . . .

(ii) The conversion of phenylmethanol to benzenecarbaldehyde has a yield of 86 %. Calculate the mass of benzenecarbaldehyde that could be produced from 10.0 g of phenylmethanol.

[3]

(iii) The ^{1}H NMR high resolution spectrum of cinnamic acid contains peaks in the area 7.0-7.5 with an area of 5 due to the benzene ring. Describe what other features you would expect to see in the spectrum. [4]

Total [13]

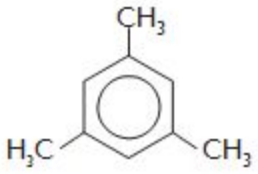
5. (a) Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions.

[6] QWC [2]

(b) Methylbenzene can be made by the Friedel-Crafts alkylation of benzene.Give the equation for this reaction and name a catalyst that can be used.

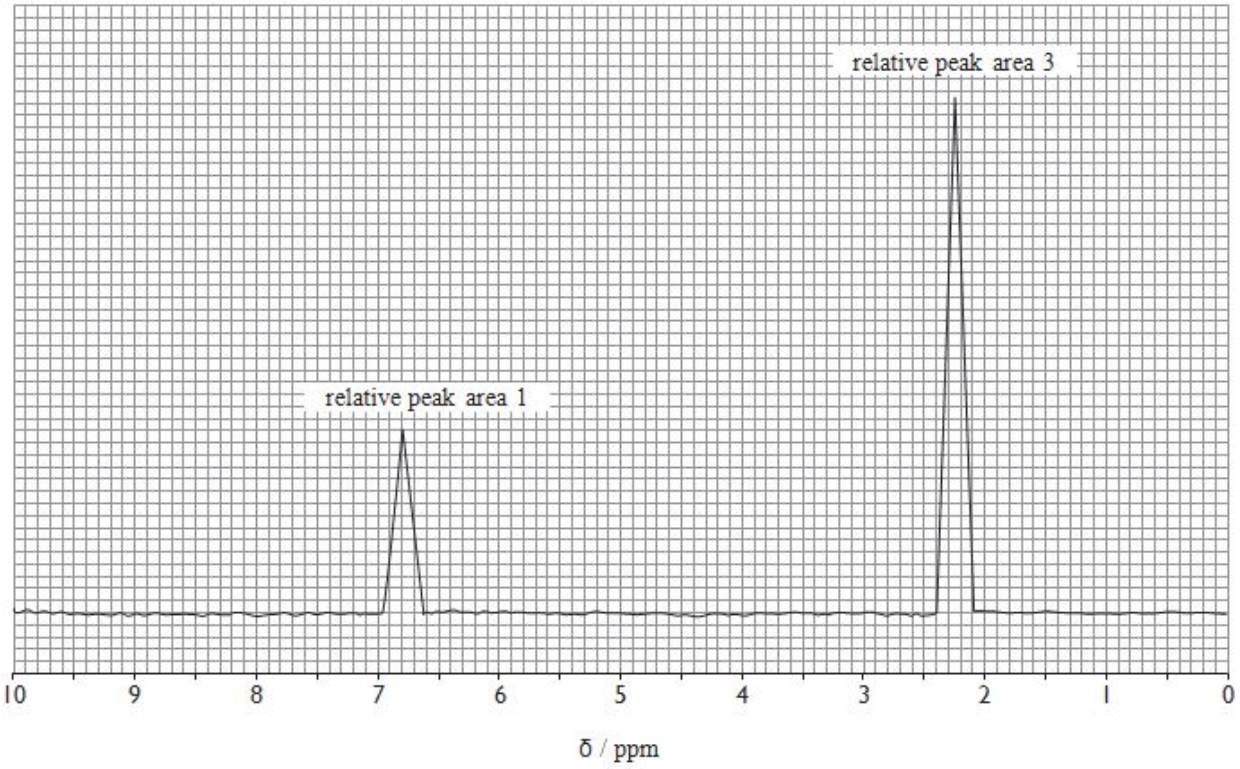
[2]

(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.

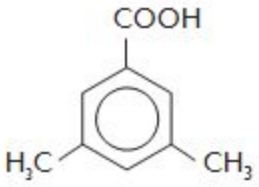


(i) The NMR spectrum of mesitylene is shown opposite.Use the chemical formula to help you explain the peaks in this spectrum, including the relative peak areas and the absence of splitting

[3]



(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



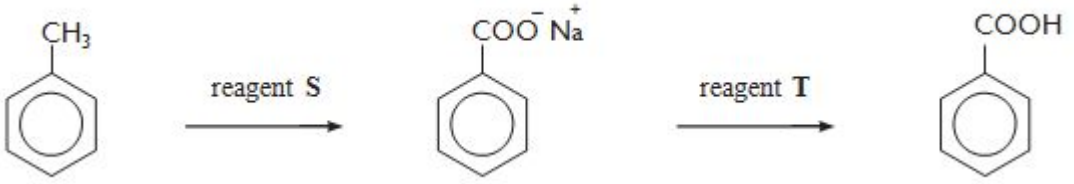
melting temperature 172 °C

Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water.

[4]

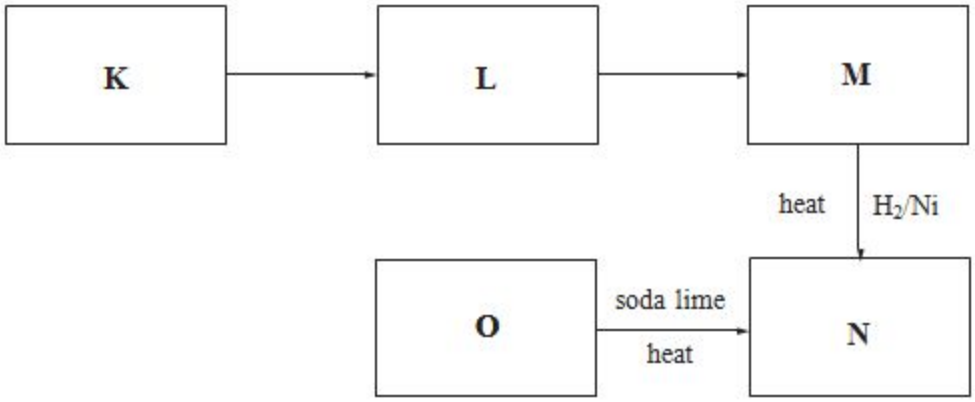
(iii) The oxidation of methylbenzene to benzenecarboxylic acid needs stronger oxidising conditions than are required for the oxidation of mesitylene. State the reagents **S** and **T** necessary for this reaction.

[2]



(Total 20)

6. *(a)* Study the reaction scheme shown below and the other information about compounds **K–O** that follows:



Compound **K** has a relative molecular mass of 58.06. It gives an orange-yellow solid with 2, 4-dinitrophenylhydrazine and gives a positive triiodomethane (iodoform) test.

0.500 g of compound **O** in aqueous solution requires 56.75 cm^3 of sodium hydroxide solution of concentration 0.100 mol dm^{-3} for complete neutralisation.
Compound **O** reacts with sodium hydroxide in a 1:1 molar ratio.

Compound **L** cannot be oxidised to compound **O**.

(i) Calculate the relative molecular mass of compound **O**. [2]

(ii) Identify compounds **K** and **O**, giving your full reasoning. [5]

(iii) Identify compounds **L**, **M** and **N**. [3]

(iv) State the reagent(s) needed for the conversion of **L** to **M**. [1]

(b) Rhodri prepared benzenecarboxylic acid, C_6H_5COOH, by hydrolysing ethyl benzenecarboxylate, $C_6H_5COOC_2H_5$.

The overall equation for this hydrolysis is:

$$C_6H_5COOC_2H_5 + H_2O \longrightarrow C_6H_5COOH + C_2H_5OH$$

He used the following method.

- Dissolve 3.20 g of sodium hydroxide in water and make up to 40.0 cm^3.
- Add the aqueous sodium hydroxide to 2.90 cm^3 of ethyl benzenecarboxylate in a round bottomed flask and reflux for 30 minutes.
- Transfer the mixture into a beaker and add dilute sulfuric acid until the solution is acidic.
- Filter the crystals obtained and recrystallise the benzenecarboxylic acid by dissolving in the minimum amount of hot water.

At the end of the experiment Rhodri's yield of benzenecarboxylic acid was 1.45 g.

(i) Suggest why Rhodri had to add sulfuric acid before recrystallising.

[1]

(ii) State why water is a suitable solvent for the recrystallisation.

[1]

(iii) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide used.

[2]

(iv) The density of ethyl benzenecarboxylate is 1.06 g cm-3. Calculate how many moles of ethyl benzenecarboxylate were used.

[2]

(v) Calculate the percentage yield obtained by Rhodri.

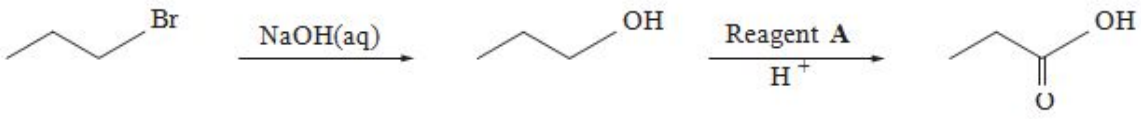
[2]

(vi) Give a reason why the percentage yield was substantially lower than 100 %.

[1]

(Total 20)

7. *(a)* 1-bromopropane can be used to prepare propanoic acid in a two-stage process shown below.



(i) Classify the reaction occurring in the first stage of this process.

[1]

(ii) The first stage uses aqueous sodium hydroxide. Under alternative conditions, 1-bromopropane produces a different product when it reacts with sodium hydroxide.

Give the alternative conditions required, and the product that would be formed from 1-bromopropane under these conditions.

[2]

(iii) For the second stage, state the **full name** of reagent **A** and classify the reaction occurring.

[2]

(iv) Reagent **A** can also be used to produce propanal from propan-1-ol. State how you would isolate propanal from this reaction

[1]

(b) (i) 1-bromopropane can also be used to prepare butanoic acid in a different two-stage process. For **each** of these two stages, give reagents and conditions required, and draw the **displayed** formula (showing all bonds) of the intermediate.

[3]

(ii) Butanoic acid is used to prepare esters used in the flavouring and perfume industries. It may be prepared from 1-bromopropane in a two-stage process as in *(b)* (i) above or from butan-1-ol or butanal in a one-stage process.

Suggest **two** factors that a scientist would consider in choosing between these different routes to produce butanoic acid on a bulk scale.

[2]

(c) Compound **B** is an isomer of formula $C_4H_8O_2$ which exists as a sweet-smelling liquid at room temperature.

(i) Elemental analysis of compound **B** shows that it has a composition of 54.5 % carbon, 9.1 % hydrogen and 36.4 % oxygen, by mass. Show that this composition is consistent with the formula above. [2]

(ii) Compound **B** shows three resonances in its H nuclear magnetic resonance spectrum.

- A triplet at 1.0 ppm with an area of 3
- A singlet at 2.1 ppm with an area of 3
- A quartet at 4.0 ppm with an area of 2

The infrared spectrum of compound **B** shows absorptions at 2981 cm^{-1} and 1750 cm^{-1}.

These are the only significant absorptions above 1500 cm^{-1}.

Using **all** the information supplied, deduce the structure of compound **B**.

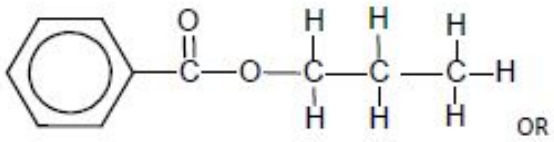
Give **reasons** in support of your answer.

[5] QWC [2]

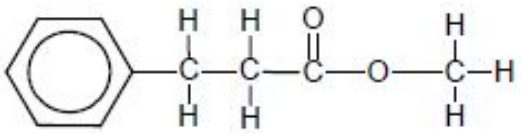
(Total 20)

3 (a) Any valid ester structure with formula $C_{10}H_{12}O_2$ [1]

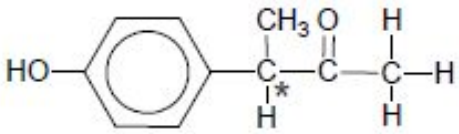
Examples:



OR



(b) (i) Compound X [1]

(ii)  [1]

(iii) Rotate the plane of polarised light in opposite directions [1]

(c)

Reagent(s)	*Observation if the test is positive*	*Compound(s) that would give a positive result*
I_2 / NaOH (aq)	Yellow solid	X
Na_2CO_3 (aq)	Bubbles of colourless gas / effervescence	W
$FeCl_3$ (aq)	Dark purple/blue/green - do not accept 'precipitate'	X, Z

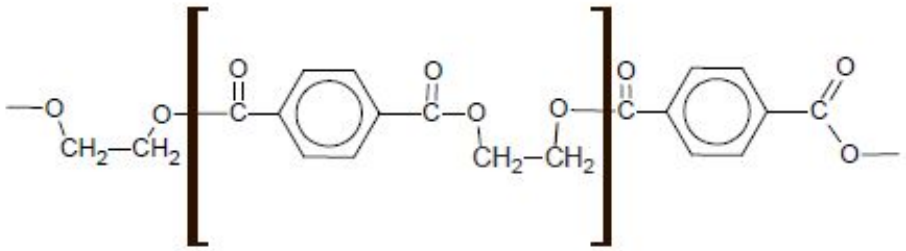
(1 mark for each box) [6]

(d) (i) Heat / Alkaline / Potassium manganate(VII) / then acidify
(1 mark for Potassium manganate + 1 other point; 2 marks for all) [2]

(ii) I. Addition polymer – One large molecule formed only / Condensation polymer – one large molecule with small molecules (e.g. water) lost. (1)

Addition polymer – one starting material / Condensation – two starting materials
OR Addition polymer – one functional group in each molecule/ Condensation polymer – two functional groups in each molecule (1) [2]

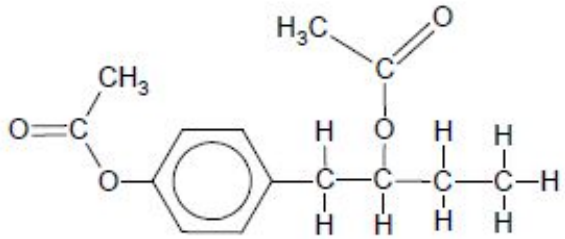
II.



[1]

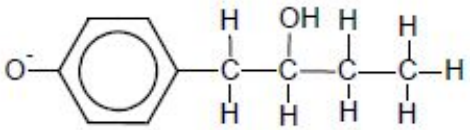
(e) (i) $NaBH_4$ / $LiAlH_4$ or name(1) Reduction (1) [2]
- ignore conditions unless $LiACH_4$ in water
- do not accept 'redox'

(ii)



Accept structures with only one –OH group reacted. [1]

(iii) [1]



[19 marks]

4 (a) Chromophore [1]

(b) (i) Melting temperature **lower** than literature value / melting occurs over a temperature range [1]

(ii) Identify percentage or amount of impurities (1)
Identify the number of compounds present or number of impurities (1) [2]

(c) (i) Acidified potassium dichromate (1)
Heat and distil (1) do not accept 'reflux' [2]

(ii) M_r of phenylmethanol = 108.08 M_r of benzenecarbaldehyde = 106.06 (1)
100% conversion would be 10.0 ÷ 108.08 × 106.06 = 9.815g (1)
86% yield = 9.815 × 86 ÷ 100 = 8.44g (1) [3]

(iii) Two resonances in the range 5.8-7.0 ppm (1)
These are doublets (1)
One **singlet** at around 11.0 ppm (1)
All resonances have the same area (1) [4]

Total [13]

5 (a) Benzene is a compound whose molecules contain six carbon atoms bonded in a (hexagonal) ring (1)
All the carbon to carbon bond lengths are equal / intermediate (1)
Each carbon atom is bonded to two other carbon atoms and a hydrogen atom (1)
by σ-bonds (1)
All the C – $\hat{C}$ – C angles are the same / 120° (1)
The remaining p electron of each carbon atom / overlap of p orbitals forms a delocalised cloud of electrons / π-system (1) above and below the plane (1)
Credit can be gained from labelled diagram
[*Candidates can gain a maximum of (4) for this part*]

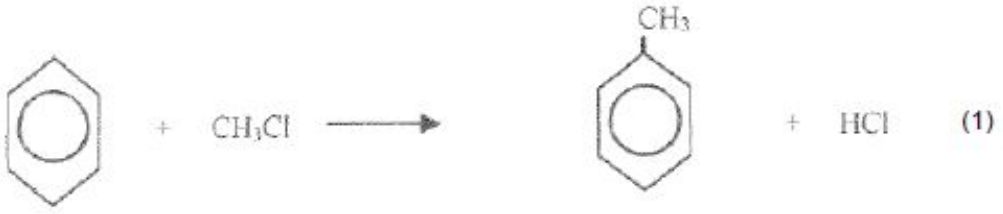
This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)
The π-cloud is **electron rich** and will be attracted to electron deficient electrophiles (1)
[*Candidates can gain (2) for this part*]

[6]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1)

Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1) *QWC* **[2]**

(b)



(1)

catalyst eg $AlCl_3$ (anhydrous) (1) **[2]**

(c) (i) (There are two environments for the protons), the 3 aromatic protons at ~6.8 δ and the 9 methyl / aliphatic protons at ~ 2.3 δ (1)
These give a peak area of 3:9, ie.1:3 (1)
These environments are separate / discrete (1) therefore no splitting pattern

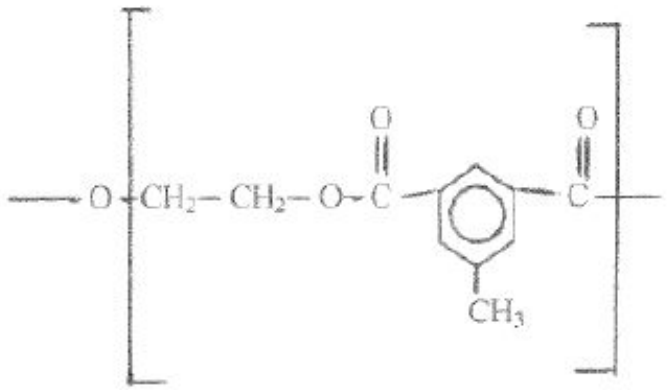
[3]

(ii) Dissolve in the minimum volume (1)
Of hot water (1)
(Filter hot) (1)
Cool (1)
Filter (1)
Dry (1)

(*up to 4 max but candidates must give the first two points in order to gain full credit*)

[4]

(iii)



[1]

(iv) Reagent **S** is alkaline potassium manganate(VII) (1)

Reagent **T** is eg hydrochloric acid (1)

[2]

Total [20]

6 (a) (i) Moles NaOH = 5.675×10^{-3} (1)

M_r O = $\frac{0.50}{0.005675}$ = 88.1 (1) [2]

(ii) **K** contains C=O due to 2, 4-dinitrophenylhydrazine reaction (1)

Contains CH_3CO due to positive iodoform test (1)

From M_r **K** must be CH_3COCH_3 (1)

O contains COOH due to neutralisation / decarboxylation reaction (1)

From M_r O must be $CH_3CH_2CH_2COOH$ / $(CH_3)_2CHCOOH$ (1) [5]

(iii) **L** is $CH_3CH(OH)CH_3$ (1)

M is C_3H_6 (1)

N is C_3H_8 (1) [3]

(iv) Concentrated H_2SO_4 / Al_2O_3 / concentrated H_3PO_4 [1]

(b) (i) To form the acid from the salt / to precipitate the acid / the salt is water soluble [1]

(ii) The acid is soluble in hot water but insoluble in cold water [1]

(iii) Moles = 3.2/40 = 0.08 (1)

Concentration = 0.08/0.04 = 2 mol dm^{-3} (1) [2]

(iv) Mass = 2.90 x 1.06 = 3.074 g (1)

Moles = 3.074/150.1 = 0.0205 (1) [2]

(v) Maximum mass = 0.0205 x 122 = 2.50 g (1)

% yield = 1.45/2.50 = 58.0% (1) [2]

(vi) Hydrolysis not complete / equilibrium forms / C_6H_5COOH slightly soluble in water / two stages so some loss at both / mass lost during recrystallisation [1]

Total [20]

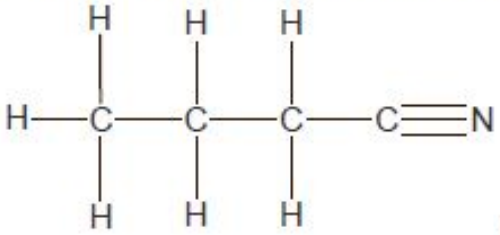
7 (a) (i) Nucleophilic substitution / Hydrolysis [1]

(ii) Dissolved in alcohol (1) Propene or unambiguous structure (1) [2]

(iii) Potassium manganate(VII) / Potassium dichromate(VI) - must be name (1)
Oxidation (1) [2]

(iv) (Add Potassium dichromate(VI)) and distil off the propanal from the reaction mixture [1]

(b) (i) Step 1: Potassium cyanide in ethanol / Heat (1)
Step 2: Heat with aqueous hydrochloric acid (or other acid) (1)



(1) [3]

(ii) Two points from different bullet points – 1 mark each.

- Atom economy / Amount of waste / Whether waste material was recyclable / Whether waste was toxic.
- Amount of energy required / temperature required / pressure required / conditions used
- Rate of production / time
- Availability of catalyst
- Cost of reactants / Availability of reactants / toxicity of reactants.
- Two step processes usually have lower yields than one step processes / percentage yield [2]
- Purification method / separation

(c) (i) Butanoic acid is $C_4H_8O_2$ so $M_r = 88$ (1)
Percentage carbon = 48/88 x 100 = 54.5%; percentage hydrogen = 8/88 = 9.1%;
Percentage oxygen = 32/88 = 36.4% (At least two of these for 1)
OR empirical formula for butanoic acid = C_2H_4O (1) and
calculate empirical formula from percentage masses = C_2H_4O (1) [2]

(ii) Structure 1 mark + 4 marks for explanations.

- Product is ethyl ethanoate. (1)
- Two points from the following required for each mark– MAX 4 marks
  - Sweet-smelling = ester
  - Peak at 1.0ppm implies – CH_3
  - Peak area 3 = CH_3
  - Peak area 2 = CH_2
  - Triplet shows CH_3 is next to a CH_2 group.
  - Singlet shows CH_3 no hydrogen atoms bonded to adjacent carbon.
  - Peak at 2.1 ppm suggests this is next to C=O.
  - Quartet shows CH_2 is adjacent to a CH_3 group.
  - Peak at 4.0 ppm shows it is –O-CH_2-
  - IR Peak at 1752 cm^{-1} = C=O
  - IR Peak at 2981 cm^{-1} = C-H or O-H
  - Cannot be –OH as we know there is no –OH in NMR spectrum

[5]

QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter. (1)

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate. (1) [2]

[20 marks]