3. *Read the passage below and then answer the question in the spaces provided.*

Carboxylic acids and their esters – versatile materials in industry and in the home

The simplest carboxylic acid, methanoic acid, occurs naturally in stinging nettles and is also used by ants and bees as a form of defence and attack. However, methanoic acid is otherwise limited in its use because of its toxicity, and there is a greater demand for ethanoic acid.

An aqueous solution of ethanoic acid (vinegar) can be made by the atmospheric oxidation of aqueous ethanol using certain bacteria.

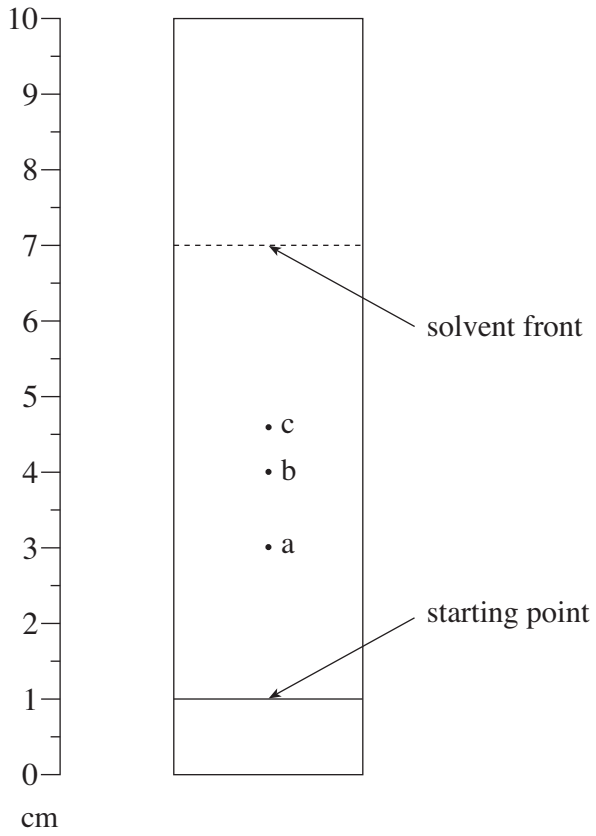
One industrial method for the production of ethanoic acid is to react methanol and carbon monoxide at a temperature of 450 K and a pressure of 30 atmospheres, in the presence of a suitable catalyst. The methanol and carbon monoxide have to be produced from coal, oil or natural gas. The process gives a 99% yield of ethanoic acid.

$$CH_3OH + CO \rightleftharpoons CH_3COOH$$

Another industrial process uses the naphtha fraction from petroleum. This process also requires increased temperatures and pressures. Unfortunately, the yield of ethanoic acid is less than 50% and a number of co-products are produced. These include methanoic, propanoic and butane-1,4-dioic acids, as well as propanone.

Esters of carboxylic acids that have a higher relative molecular mass occur naturally as oils, fats and waxes, and a number of these are used in the perfume industry. Some of these esters are glycerides – esters derived from propane-1,2,3-triol (glycerol). Alkaline hydrolysis of these glycerides produces sodium or potassium salts of large-molecule carboxylic acids that are used as soaps. Many of these oils, fats or waxes contain glycerides of a number of different carboxylic acids and the separation and identification of these is difficult.
One method of identification is to convert the glyceryl esters to simple ethyl esters and then to separate and identify the ethyl esters by thin layer chromatography (TLC).

A typical TLC chromatogram is shown below.



Man-made esters have been developed to have specific uses. For example, the polymer PET is
25 used to make bottles and in textiles such as *terylene*, whereas polyvinyl acetate (PVA) is used as an adhesive.

- End of passage -

Examiner only

(a) By law, the concentration of ethanoic acid present in vinegar has to be within certain limits.

$50.00\,cm^3$ of a sample of vinegar was diluted to exactly $500\,cm^3$ by the addition of distilled water, using a volumetric flask.
$25.00\,cm^3$ of this **diluted** solution was exactly neutralised by $26.25\,cm^3$ of a solution of sodium hydroxide of concentration $0.100\,mol\,dm^{-3}$.

(i) State a procedure that is essential when diluting a solution, so that the results of the titration are accurate. [1]

.....

(ii) Use this information and the equation below to calculate the concentration of ethanoic acid present in the **undiluted** vinegar in mol dm^{-3}. [4]

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

.....

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(b) The passage describes two industrial methods for making ethanoic acid *(lines 6 to 14)*. These are summarised in the table below.

Method	Starting materials	Temp / K	Pressure / atmosphere	Yield of ethanoic acid / %
1	methanol, carbon monoxide	450	30	99
2	naphtha from petroleum	450	50	< 50

Examiner only

Use the information in the passage and in the table to discuss the relative advantages and disadvantages of **each** process. [4]

(QWC) [1]

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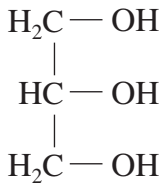
(c) The formulae of glycerol (propane-1,2,3-triol) and lauric acid (dodecanoic acid) are given below.



glycerol

$CH_3(CH_2)_{10}COOH$

lauric acid

Write the structural formula of the tri-ester, glyceryl trilaurate, formed by the reaction of glycerol and lauric acid.

You need not show the bonds between carbon and hydrogen atoms in your answer. [1]

(v) Ketones, such as propanone, can be identified by using 2,4-dinitrophenylhydrazine.
In a test, a few drops of a compound suspected to be propanone were added to a solution of 2,4-dinitrophenylhydrazine.
Describe what was seen and how the product of this test could be used to positively identify the compound as propanone.

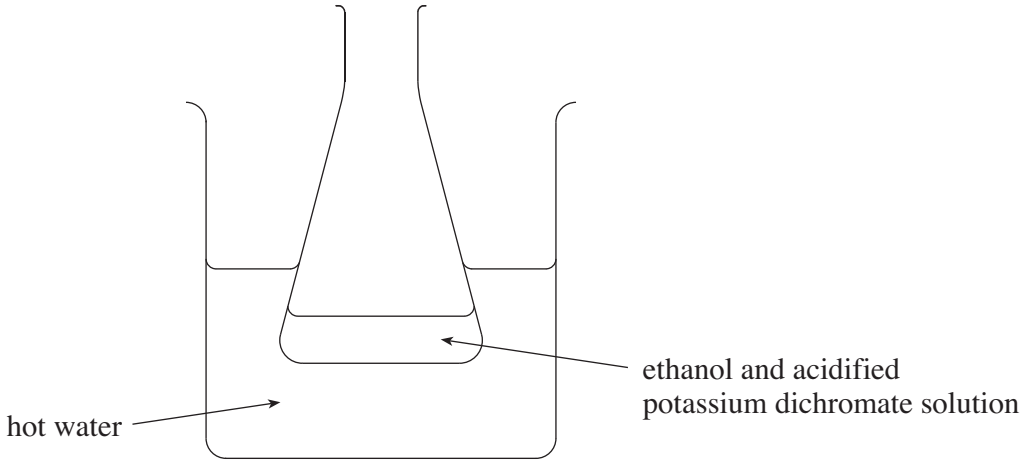
You should assume that any compound produced has been separated and purified. [3]

(vi) In analytical laboratories, compounds can be separated by gas chromatography and identified by mass spectroscopy.

An impure sample of propanone was obtained in this way and its mass spectrum showed the presence of another ketone, **T**, which showed a molecular ion peak, M^+, at m/z 86.
In addition, other significant peaks were seen at m/z values of 29 and 57.
Use this information to show that **T** could be pentan-3-one. [3]

Total [20]

(c) A few cm^3 of ethanol were added to an acidified solution of potassium dichromate in a small flask and placed in a water bath at 60°C.



(i) State what would be seen if the mixture was left for a period of time and explain why this change would occur. [2]

(ii) Pure samples of the organic products were then isolated.
State the names of the organic products and give a chemical test for **each** one, including the expected observations. [4]

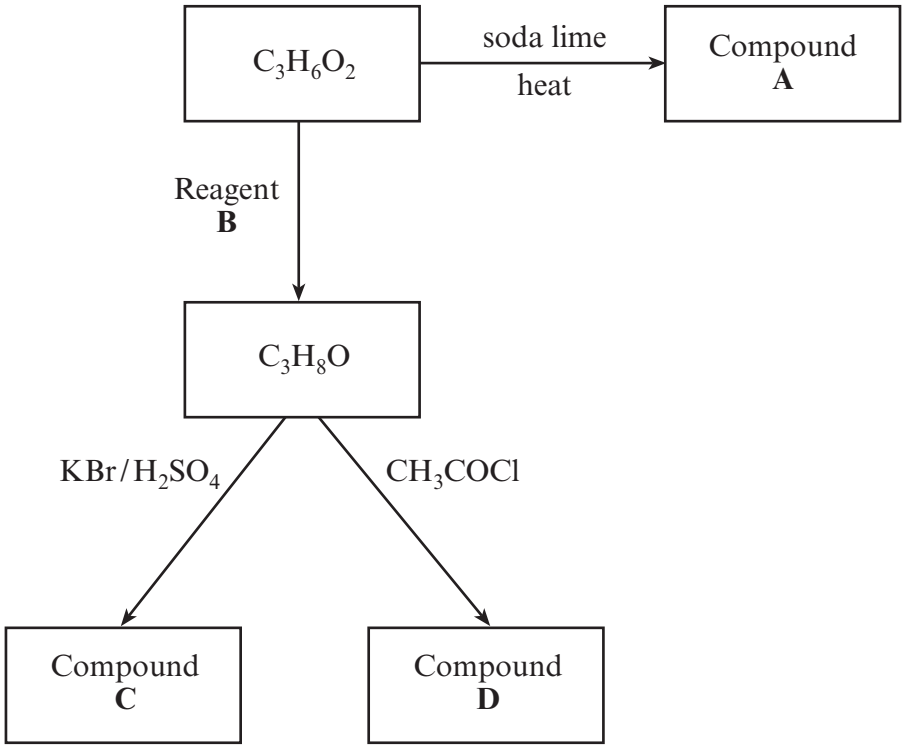
(QWC) [1]

Total [20]

Section B Total [40]

Examiner only

(b) Study the reaction scheme shown below:



(i) State the name of compound **A**. [1]

.....

(ii) Give the formula of reagent **B**. [1]

.....

(iii) Draw the displayed formula of compound **C**. [1]

(iv) State the **name** of compound **D**. [1]

.....

Total [10]

Examiner only

2. *(a)* Explain the difference in structure between *primary* and *secondary* alcohols. [1]

.....

.....

(b) Quantitative analysis of an alcohol shows that its percentage composition by mass is C 68.1%, H 13.7% and O 18.2%. It has a relative molecular mass of 88.1.

Calculate the empirical formula of the alcohol and show that its molecular formula is the same as the empirical formula. [3]

.....

.....

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(c) The following compounds have the same molecular formula, $C_5H_{10}O$.

A $CH_3CH_2COCH_2CH_3$ **B** $CH_3CH_2CH_2CH_2CHO$

C $CH_3CH_2CHCHCH_2OH$ **D** $CH_2CHCH_2CH(OH)CH_3$

(i) Draw the structure of an isomer of **B** that is also an aldehyde. [1]

(ii) I. State which **one** of the compounds **A–D** exhibits E-Z (trans-cis) isomerism. [1]

.....

II. Draw the structures of **both** isomers. [1]

Examiner only

(iii) Give one test, including reagents and expected observations, which would distinguish between **A** and **B**. [2]

.....

.....

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.....

(iv) Give one test, including reagents and expected observations, which would distinguish between **C** and **D**. [2]

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.....

.....

(d) Ketones such as propanone react with hydrogen cyanide.

(i) Classify the type of reaction taking place. [1]

.....

(ii) Draw, with the aid of curly arrows, the mechanism for this reaction. [3]

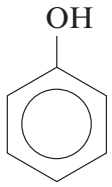
Total [15]

1094 01 07

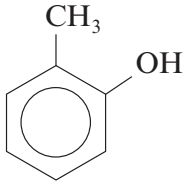
3. *Read the passage below and then answer the questions in the spaces provided.*

Phenol

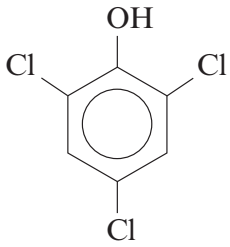
Phenol, formula C_6H_5OH, has an hydroxyl group joined directly to an aromatic ring.



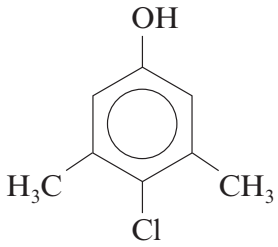
Phenol has many derivatives including 2-methylphenol.



Phenol was isolated from coal tar in 1835 and its original name was carbolic acid. It is a weak acid, between carboxylic acids and alcohols in strength. In 1865 the English surgeon Joseph Lister pioneered the use of phenol as the first surgical antiseptic and by the beginning of the 20th century phenol was commonly used as an antiseptic, but its use is not permitted today. Familiar pharmaceutical products such as TCP and Dettol are much more effective as antiseptics and disinfectants and do not have the toxicity of phenol itself.



TCP



Dettol

Nowadays most phenol is produced by the cumene process with less than 5% being made from coal tar. Recently a new process has been developed where phenol is made by the direct oxidation of benzene using nitrous oxide, N_2O, as the oxidising agent. This reaction could be of particular value since N_2O, a pollutant under strict control, is a by-product of the production of hexanedioic acid used to make nylon-6,6. The new process provides a very high yield of phenol and produces no significant aqueous waste products.

Phenol is very important since it is used in the production of

- epoxy and polycarbonate resins (e.g. as adhesives, in safety glasses and in drinking bottles),
- nylon,
- phenolic resins (e.g. as plywood adhesive, in fibreglass and in moulded electrical components),
- derivatives of ethanoic anhydride.

You would be unwise to handle phenol, but it is a key chemical in the manufacture of many everyday materials you do handle.

– End of passage –

Examiner only

(a) Describe a chemical test to show the presence of the –OH group in 2-methylphenol (line 4) by giving the reagent(s) and observation(s).

Reagent(s) ..... [1]

Observation(s) ..... [1]

(b) Explain why phenol is more acidic than alcohols but less acidic than carboxylic acids (line 6). [4]

.....

.....

.....

.....

.....

.....

(c) Give the systematic name of Dettol (line 11). [1]

.....

(d) The new process for the production of phenol (line 13) can be represented by the following equation.

$$C_6H_6 + N_2O \longrightarrow C_6H_5OH + N_2$$

Calculate the atom economy of the reaction. [2]

.....

.....

.....

.....

Examiner only

(e) Draw the displayed formula of hexanedioic acid (line 16). [1]

(f) State the name of a compound that can react with hexanedioic acid to form nylon-6,6. [1]

.....

(g) Draw the repeating unit in nylon-6,6 (line 16). [1]

(h) Nylon-6,6 is a typical example of a condensation polymer. Explain the difference between condensation polymerisation and addition polymerisation. [2]

.....

.....

.....

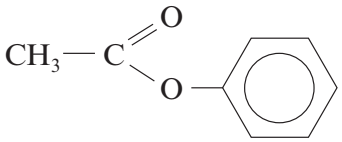
(i) Give **one** important industrial use of ethanoic anhydride. [1]

.....

Total [15]

Total Section A [40]

(d) The reaction between phenol and ethanoyl chloride gives the aromatic compound **W**.

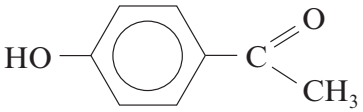


compound **W**

(i) State the name of the group of compounds to which compound **W** belongs. [1]

.....

(ii) Using a suitable catalyst, compound **W** can rearrange to give compound **Y**.



compound **Y**

Compound **Y** gives a positive triiodomethane (iodoform) test.
State the reagents used for this test and what is observed. [2]

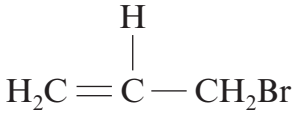
Reagents .....

Observation .....

Total [13]

Examiner only

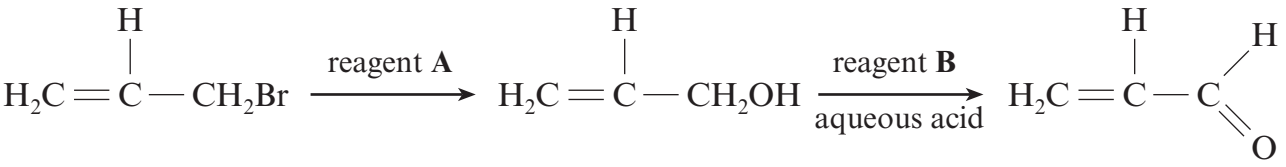
2. *(a)* Allyl bromide is the traditional name for the compound that has the following formula.



(i) Give the **systematic name** for this compound. [1]

.....

(ii) Allyl bromide can be converted to acraldehyde (prop-2-en-1-al) in a two-stage reaction.



State the names of reagent **A** and reagent **B**. [2]

Reagent **A** .....

Reagent **B** .....

(b) Acraldehyde reacts with 2,4-dinitrophenylhydrazine.

(i) State the type of reaction that occurs. [1]

.....

(ii) Describe the appearance of the organic product that is produced. [1]

.....

(iii) State how the purified organic product from (ii) is used to clearly identify the starting aldehyde as acraldehyde. [1]

.....

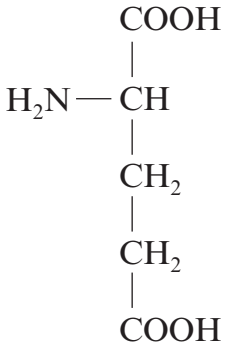
.....

(iv) The infrared spectrum of an impurity present when acraldehyde is made by the method above, shows peaks at 1725 cm^{-1} and at 2500-3550 cm^{-1}.
Suggest the displayed formula of the impurity that is responsible for these peaks and the type of reaction that has produced it from acraldehyde. [2]

Displayed formula .....

Type of reaction .....

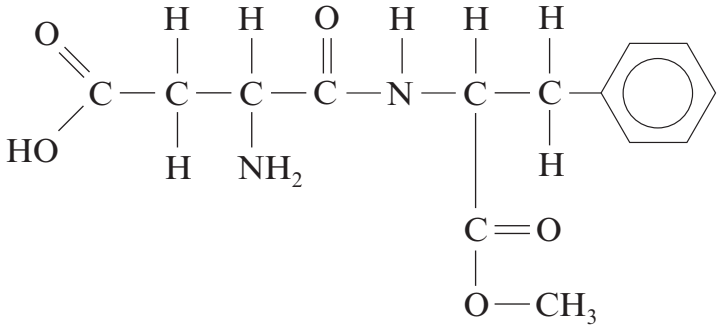
(e) MSG *(line 19)* is the monosodium salt of the α-amino acid glutamic acid.



glutamic acid

Give the **structural** formula of the organic species produced when glutamic acid is dissolved in excess alkali. [1]

(f) The artificial sweetener aspartame is a common sweetener in soft drinks. However, these should not be kept for any length of time as the **ester group** slowly hydrolyses.



aspartame

Give the structural formula of the two organic compounds produced from this hydrolysis of the ester group. [2]

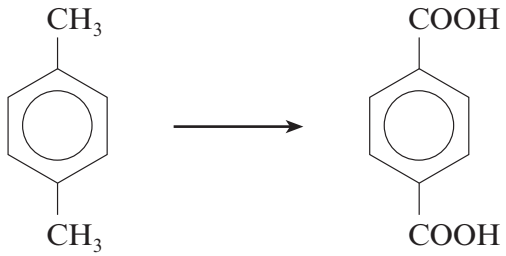
Total [15]

Section A Total [40]

(ii) The two isomers are separated by recrystallisation from ethanol, in which the 2-isomer is much more soluble.
Use the information provided to state and explain how you would know when the 4-isomer is no longer contaminated with traces of the 2-isomer. [2]

(iii) In an experiment 8.10 g of N-phenylethanamide (M_r 135) produced 6.48 g of pure 4-nitro-N-phenylethanamide (M_r 180).
Calculate the percentage yield of 4-nitro-N-phenylethanamide. [3]

(c) One stage in the preparation of the polyester PET is the oxidation of 1,4-dimethylbenzene to benzene-1,4-dioic acid.



This is carried out in the laboratory by refluxing 1,4-dimethylbenzene and an alkaline solution (containing sodium hydroxide) of an oxidising agent **G**, giving an intermediate product, which is then acidified.

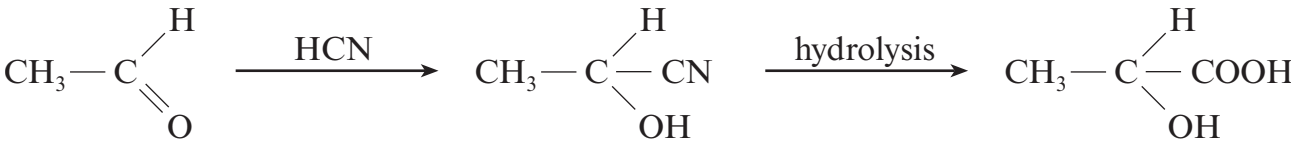
(i) State the name of oxidising agent **G**. [1]

(ii) Explain why it is then necessary to acidify the intermediate product to give the required acid. [1]

(d) The polyester PET is produced by reacting benzene-1,4-dioic acid and ethane-1,2-diol.
Draw the formula of the repeating unit found in PET and state why this reaction is described as condensation polymerisation. [2]

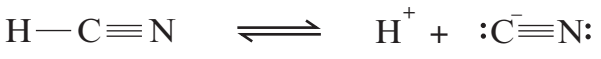
Total [20]

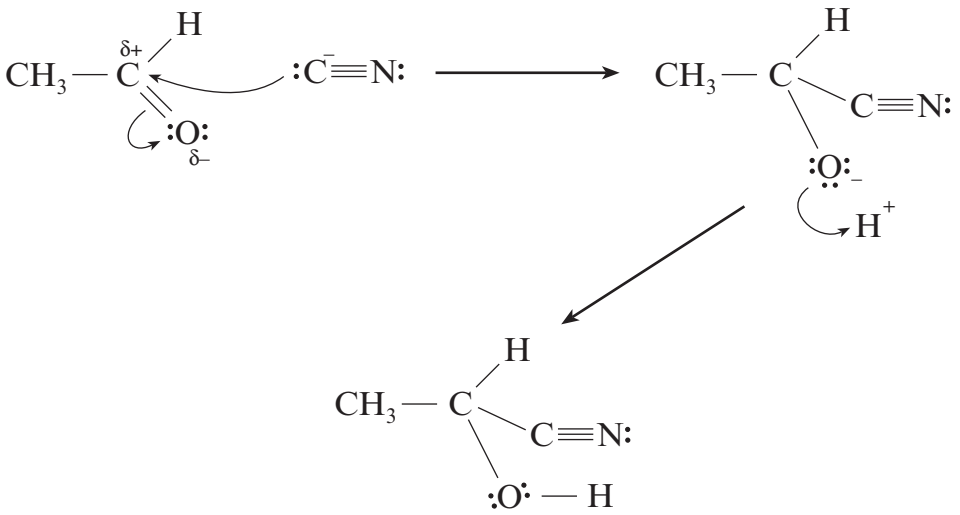
5. *(a)* 2-Hydroxypropanoic acid (lactic acid) can be made from ethanal by reaction with hydrogen cyanide and the subsequent hydrolysis of the 2-hydroxypropanenitrile.



2-hydroxypropanenitrile 2-hydroxypropanoic acid

(i) The mechanism for the reaction between ethanal and hydrogen cyanide is shown below.





Describe what is happening at each stage of this reaction mechanism and use your answer to explain why this reaction is described as nucleophilic addition. [4]

(QWC) [1]

(ii) During the second stage of the reaction 2-hydroxypropanenitrile is hydrolysed to 2-hydroxypropanoic acid.
Describe what is meant by the term *hydrolysis* and give the reagent used for this hydrolysis. [2]

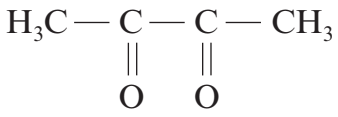
(b) (i) Yoghurt contains lactic acid that has been produced from lactose by certain bacteria.
The percentage of lactic acid in yoghurt can be found by an acid-base titration.
A sample of plain yoghurt of mass 50.0 g was titrated with sodium hydroxide solution of concentration 0.250 mol dm^{-3}. The lactic acid in the yoghurt was exactly neutralised by 20.0 cm^3 of the sodium hydroxide solution.

$$\underset{M_r\,90}{CH_3CH(OH)COOH} + NaOH \rightarrow CH_3CH(OH)COONa + H_2O$$

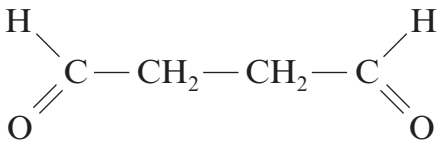
Use the information above and the equation to calculate the percentage of lactic acid present in the yoghurt. [3]

(ii) Some students suggested that it would be less wasteful if just a 10 g sample of yoghurt was used, rather than a 50 g sample, in this titration.
Explain why this would be likely to give a less accurate result. [1]

(c) Butan-2,3-dione (found in yoghurt) and butan-1,4-dial are isomers.



butan-2,3-dione



butan-1,4-dial

Describe the observations made when both compounds are tested with Fehling's reagent. [2]

(d) You are provided with the following information about aliphatic ester **T**.

- the empirical formula is $C_2H_3O_1$
- the relative molecular mass is 172
- all the oxygen atoms are present in ester groupings
- it decolourises aqueous bromine
- methanol is the only alcohol produced on hydrolysis of ester **T**
- the ^1H NMR spectrum consists of two unsplit peaks of equal size

Use **all** this information to deduce the structural formula of ester **T**, showing your reasoning. [6]

(QWC) [1]

Total [20]

Section B Total [40]

Examiner only

2. *(a)* Butan-1-ol can be produced by the reduction of butanal.

(i) State the name of a reducing agent that can be used for this reaction. [1]

.....

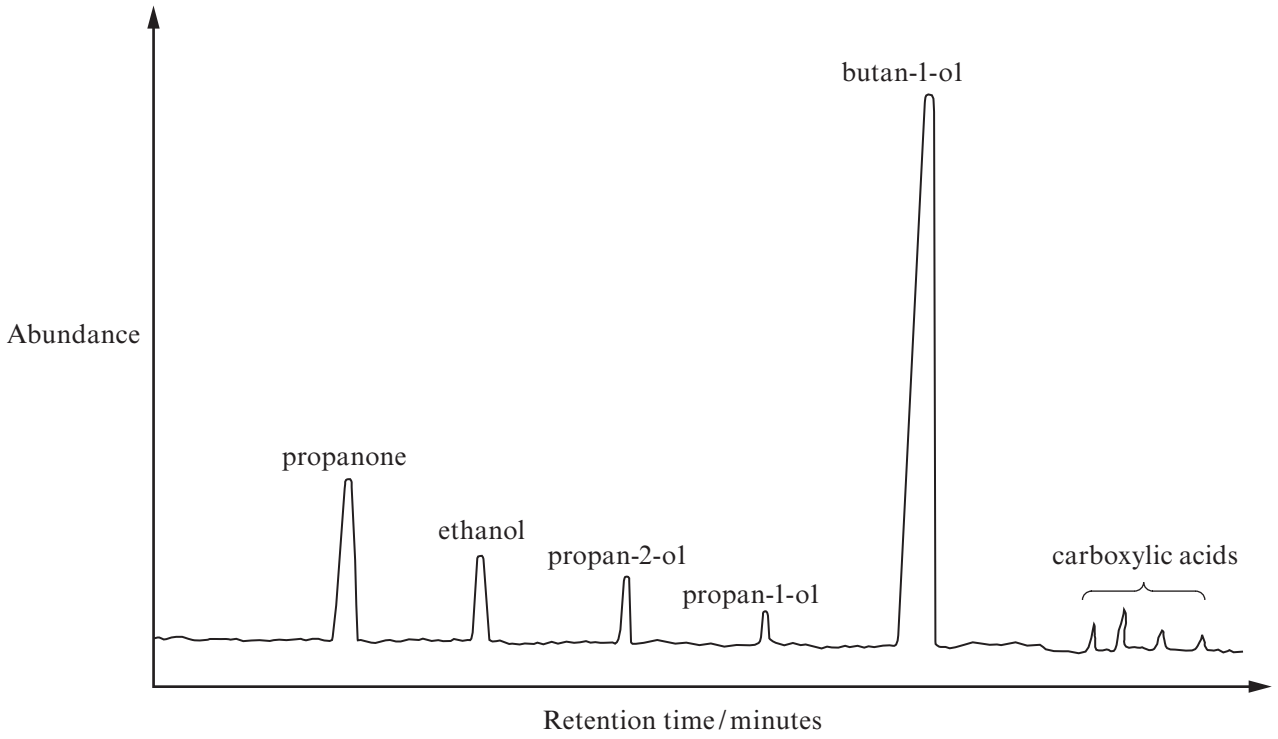
(ii) The infrared spectrum of butanal shows an absorption at 1731 cm^{-1}.
State which bond in butanal is responsible for this absorption and explain how the intensity of this absorption changes as the reduction proceeds. [2]

.....

.....

.....

(b) A traditional route for making butan-1-ol is by the fermentation of sugar cane residues and other starch-containing materials. One problem with this method is that a number of other products are also obtained.
The gas chromatogram shows the major products from a typical fermentation of starch.



Use the chromatogram to help you answer the questions below and opposite.

(i) State, in **decreasing** order of abundance, the three main products of this fermentation. [1]

....

Examiner only

(ii) State which **one** of the products in (i) **cannot** normally be oxidised to a carboxylic acid. [1]

.....

(iii) Select **two** compounds, from the chromatogram, that will give a positive result in the triiodomethane (iodoform) reaction giving an explanation for your answer. [2]

Compounds ..... and .....

Explanation .....

.....

.....

(iv) Since there is a plentiful supply of cellulose from plants, scientists are using a new bacterium to ferment cellulose rather than starch. The first results of this research have been promising.
If this new method is to be tested by other research groups why is it essential that the conditions are kept exactly the same? [1]

.....

(c) There is interest in developing butan-1-ol as a fuel to replace petrol and diesel as this would be a carbon neutral fuel.
Suggest why this fuel is described as carbon neutral, giving a reason for your answer. [2]

.....

.....

.....

(d) A large proportion of the butan-1-ol produced is used to react with ethanoic acid to produce 1-butyl ethanoate.

(i) Give the equation for this reaction. [1]

.....

(ii) State the name of the catalyst that is used. [1]

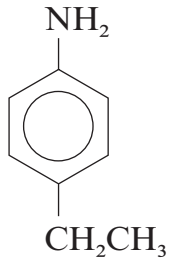
.....

Total [12]

1094 010007

(b) Explain why 2-phenylethylamine is a base. [2]

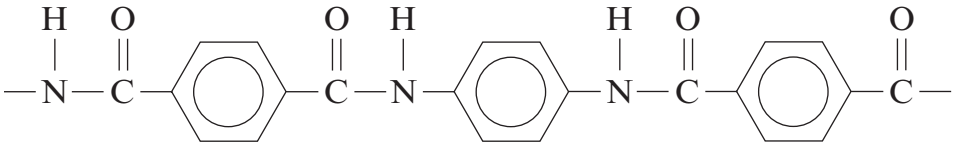
(c) State how both 2-phenylethylamine and its isomer 4-ethylphenylamine react with nitric(III) (nitrous) acid at 5°C.



4-ethylphenylamine

In **each** case you should state the type of compound produced and any relevant observations. [3]

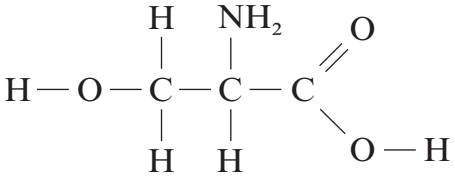
(d) Kevlar ® is a polyamide that is used in bullet-proof vests.



Kevlar ®

Give the formula of two starting materials that can be reacted together to give Kevlar ®. [2]

(e) Silk is a naturally occurring material composed of polymerised serine molecules. Serine is an α-amino acid.



serine

(i) Give the **systematic name** of serine, which is a derivative of propanoic acid. [1]

(ii) Hydrogen bonding is largely responsible for the solubility of serine in water. Explain what is meant by hydrogen bonding, using serine to illustrate your answer. [3]

(QWC) [1]

Total [20]

Section B Total [40]

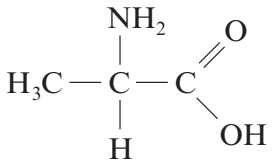
Examiner only

(b) Draw the displayed formula of the organic compound formed when lactic acid reacts with

(i) sodium hydroxide, [1]

(ii) acidified potassium dichromate. [1]

(c) Lactic acid can be formed directly from compound **H**.



compound **H**

(i) Give the **systematic** name for compound **H**. [1]

.....

(ii) State the reagent needed to convert **H** into lactic acid. [1]

.....

(iii) Explain why compound **H** has a much higher melting temperature than lactic acid. [2]

.....

.....

.....

Total [12]

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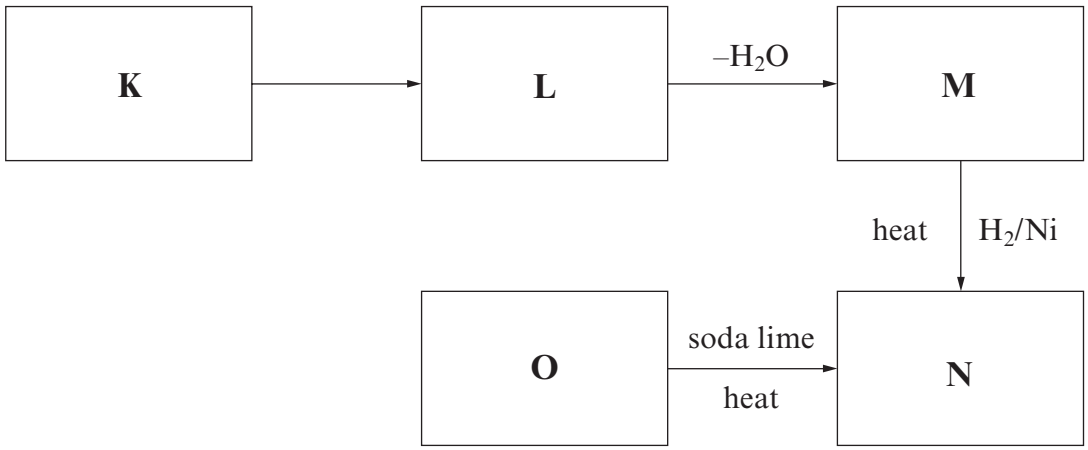
SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(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]

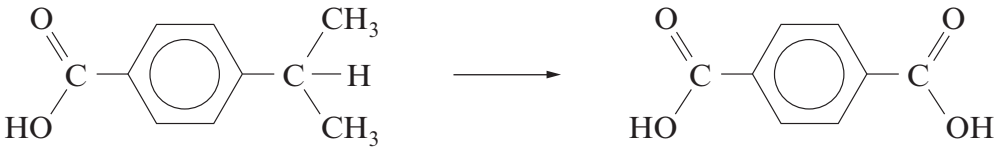
Examiner only

(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 reaction. [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]

.....

.....

.....

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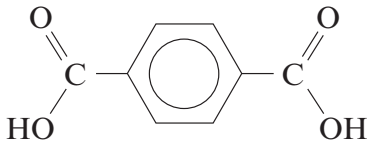
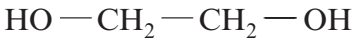
II. Draw the repeat unit for the polymer formed between benzene-1,4-dioic acid and ethane-1,2-diol. [1]

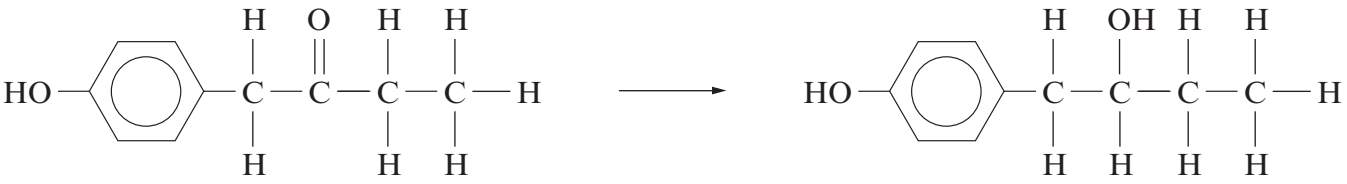


benzene-1,4-dioic acid
(terephthalic acid)



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 .....

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(b) Give **one** use of proteins or polypeptides in biological systems. [1]

.....

(c) One laboratory synthesis of amino acids involves the reaction between an aldehyde and hydrogen cyanide, HCN, as the first step before the amino group is introduced into the molecule.
For a general aldehyde, R-CHO, draw the mechanism of the reaction that occurs between this molecule and HCN. [3]

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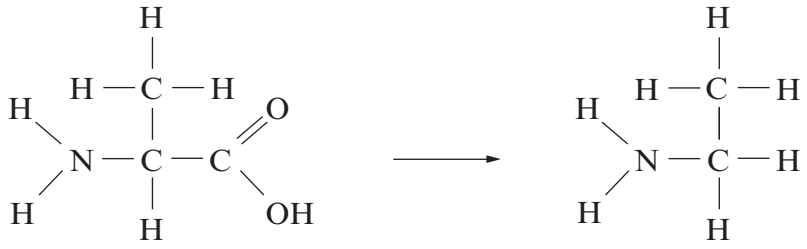
(d) Amino acids can be converted to amines in a one-step process, as shown below.

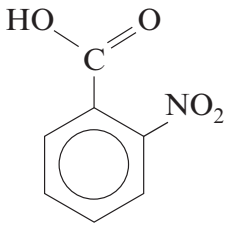


Name the reagent required for this reaction. [1]

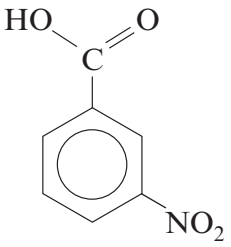
.....

Total [10]

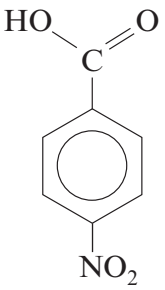
5. *(a)* Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



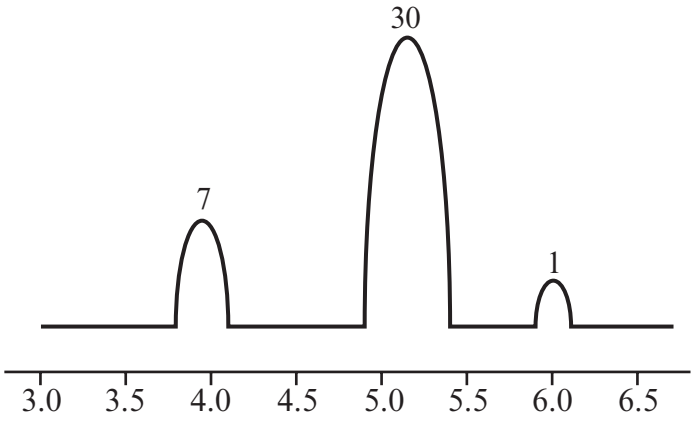
3-nitrobenzoic acid



4-nitrobenzoic acid

(i) Benzenecarboxylic acid can be nitrated under similar conditions to the nitration of benzene.
Give the reagent(s) and condition(s) required and classify the mechanism of this reaction. [3]

(ii) Nitration of benzenecarboxylic acid gives a mixture of products. These can be identified by gas chromatography followed by mass spectrometry *(GC-MS)*. The gas chromatograph for the products of this reaction is shown below, with the relative areas of each peak indicated.



Retention time / minutes

I. The main isomer produced is 3-nitrobenzenecarboxylic acid.
Calculate the percentage of this isomer produced. [2]

II. The mass spectrum of 3-nitrobenzenecarboxylic acid has main peaks at m/z 45, 46, 122 and 167. Suggest which species are responsible for **each** of these peaks. [2]

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(iii) An impure sample of 3-nitrobenzenecarboxylic acid was obtained.

I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all. [1]

II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

Describe how impure 3-nitrobenzenecarboxylic acid could be purified by recrystallisation. Include full experimental details. [4]

(QWC) [1]

QUESTION 5 CONTINUES ON PAGE 16

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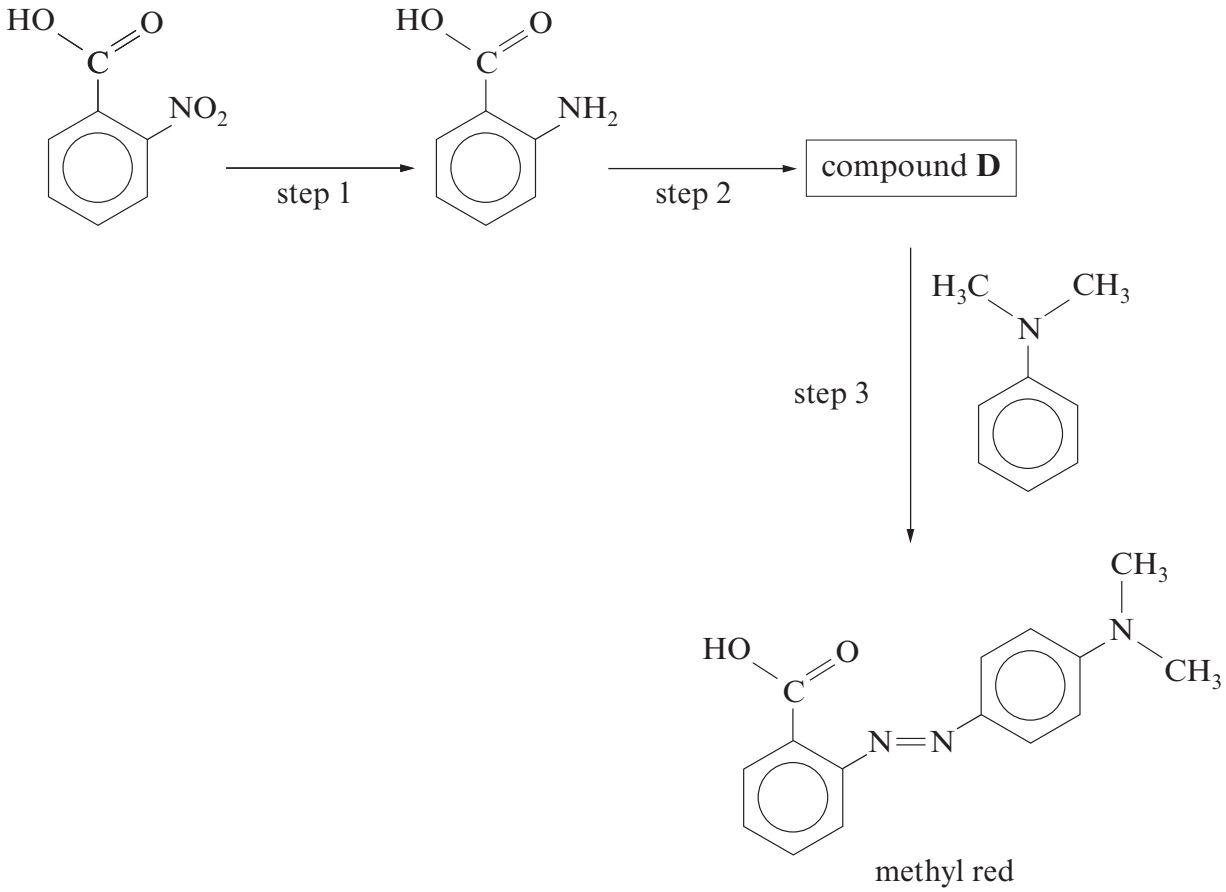
(b) 2-nitrobenzenecarboxylic acid may be used as a starting material for the production of the indicator methyl red. A reaction scheme for this process is given below.



methyl red

(i) Give the reagent(s) necessary for step 1. [1]

(ii) Step 2 uses a mixture of sodium nitrate(III), $NaNO_2$, with dilute hydrochloric acid. Give the conditions required for this reaction and the structure of the product, compound **D**. [2]

(iii) Methyl red is red below pH 4. Explain the origin of this colour. [2]

(c) Methyl red is used to differentiate between acids and bases. Explain why amines such as ethylamine are bases. [2]

Total [20]

Total Section B [40]

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SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* From the information given, draw the displayed formula of each compound.
In parts (i)-(iii) the compounds consist of molecules that have **three** carbon atoms.
In part (iv) the compound has **four** carbon atoms.

(i) A compound that is oxidised to a ketone [1]

(ii) A neutral sweet-smelling compound [1]

(iii) An α-amino acid [1]

(iv) A hydrocarbon that exhibits E–Z isomerism [1]

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2. *(a)* 2,4-Dinitrophenylhydrazine reagent (2,4-DNP), Tollens' reagent and iodine in sodium hydroxide solution can all be used in the laboratory to identify unknown compounds. Complete the table below by giving any observations made (or writing 'no reaction' as appropriate) when these reagents are added to the compounds listed. [4]

	butan-2-ol	ethanal	ethanol	propanone
2,4-DNP	no reaction			
Tollens' reagent			no reaction	
I_2/NaOH				

(b) Under certain conditions ethanol can be formed from ethene and water. A possible mechanism for this reaction is shown below.

$$CH_2{=}CH_2 + H^+ \longrightarrow CH_3CH_2^+ \xrightarrow{H_2O} C_2H_5OH + H^+$$

(i) Classify this type of mechanism. [1]

.....

(ii) State the name given to species such as the intermediate ion $CH_3CH_2^+$. [1]

.....

(iii) Give another reaction of ethene that follows this type of mechanism. [1]

.....

(iv) Give a reason why the main product of the reaction between propene and water under similar conditions is propan-2-ol. [1]

.....

.....

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(c) Propanone can react with hydrogen cyanide.

(i) Classify the type of reaction taking place when propanone reacts in this way. [1]

.....

(ii) Draw the mechanism for this reaction. [3]

Total [12]

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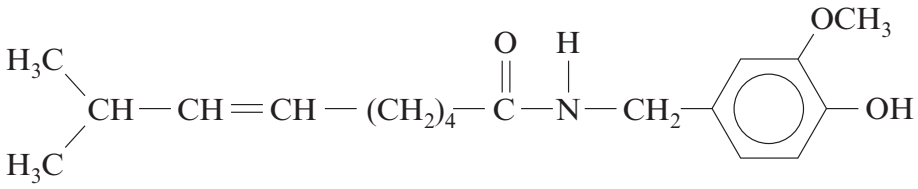
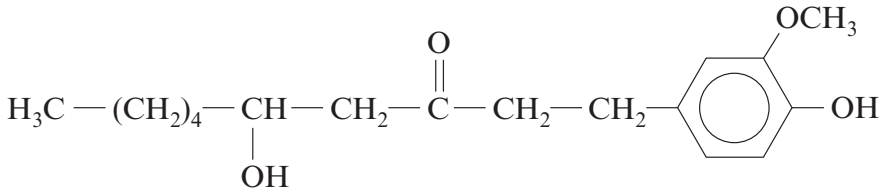
Pungency

One group of compounds that produce a sensation of pungency or heat contain an aromatic ring system carrying two oxygen atoms. This seems to be the key structure responsible for their
25 interaction with the taste buds. Two examples are shown below.



capsaicin (chilli peppers)



gingerol (ginger)

– End of passage –

(a) Describe what is meant by hydrogen bonding, using an example of your choice. [3]
QWC [1]

.....

.....

.....

.....

.....

.....

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(e) Calculate the minimum concentration of MSG, in mol dm^{-3}, which if added to clear soup makes its 'pleasantness score' rapidly fall *(lines 20-21)*. [2]

Minimum concentration = ... mol dm^{-3}

(f) Giving the reagent(s) and an observation, state a chemical test that gives a positive result with both capsaicin and gingerol *(lines 26-27)*. [2]

Reagent(s) .....

Observation .....

(g) Giving the reagent(s) and an observation, state a chemical test that gives a positive result with gingerol but **not** with capsaicin. [2]

Reagent(s) .....

Observation .....

Total [14]

Total Section A [40]

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(b) The oxidation of tertiary alcohols is different from those of primary and secondary alcohols. 'Tertiary butanol' is oxidised to propanone and methanoic acid.

(i) State a test that will give a positive result for propanone but not methanoic acid. [2]

Reagent .....

Observation .....

.....

(ii) State a test, other than the use of an acid-base indicator, that will give a positive result for methanoic acid but not propanone. [2]

Reagent .....

Observation .....

.....

Total [13]

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2. *(a)* You are given two aqueous solutions in unlabelled bottles. One is methyl propenoate, $CH_2 = CHCOOCH_3$, and the other is phenol, C_6H_5OH.

Give a chemical test, other than the use of an acid-base indicator, which you could use to distinguish between these two compounds, giving the result of the test for **each** compound. [2]

.....

.....

.....

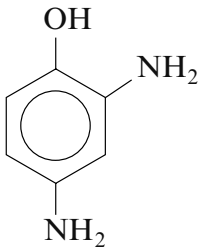
(b) 2,4-Dinitrophenol is a yellow solid that is an inhibitor of ATP production in cells. As a result it has been sold as an aid to slimming, in spite of it being a dangerous and unlicensed product.

(i) State why this compound is seen as yellow in white light. [1]

.....

.....

(ii) Reduction of 2,4-dinitrophenol, using the same reducing agent that is used for the reduction of nitrobenzene, gives the photographic developer 'amidol'.



amidol

State the reagent(s) used for this reduction. [1]

.....

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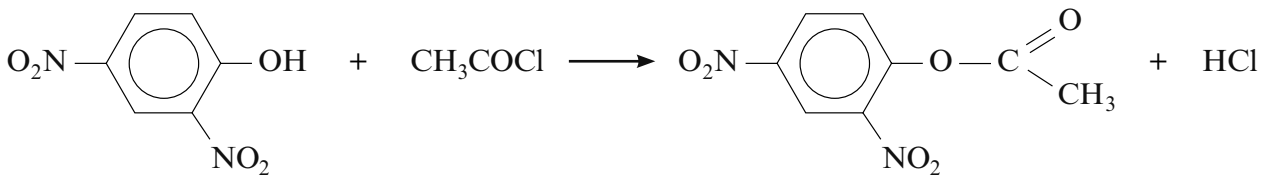
(c) (i) 2,4-Dinitrophenol reacts with ethanoyl chloride to produce 2,4-dinitrophenyl ethanoate.

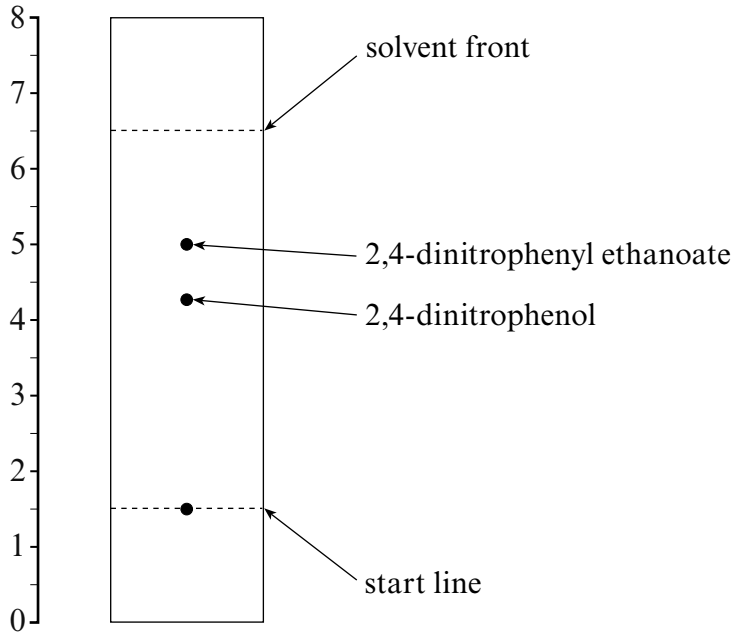


M_r = 184 M_r = 226

In an experiment 7.36 g of 2,4-dinitrophenol produced 7.91 g of 2,4-dinitrophenyl ethanoate. Calculate the percentage yield of 2,4-dinitrophenyl ethanoate. [3]

Percentage yield = ... %

(ii) The 2,4-dinitrophenyl ethanoate obtained in *(c)*(i) was impure and contained some unreacted 2,4-dinitrophenol. The presence of this phenol was detected using thin layer chromatography.



Calculate the R_f value of 2,4-dinitrophenol from this chromatogram. [2]

.....

.....

.....

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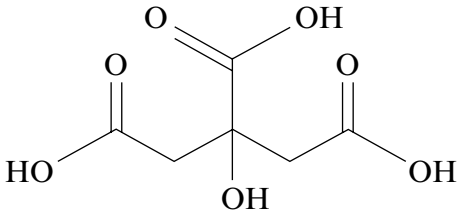
3. *Read the passage below and then answer the questions in the spaces provided.*

Citric acid – its production and chemistry

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is a weak organic acid that occurs naturally in many fruits.



$M_r = 192$

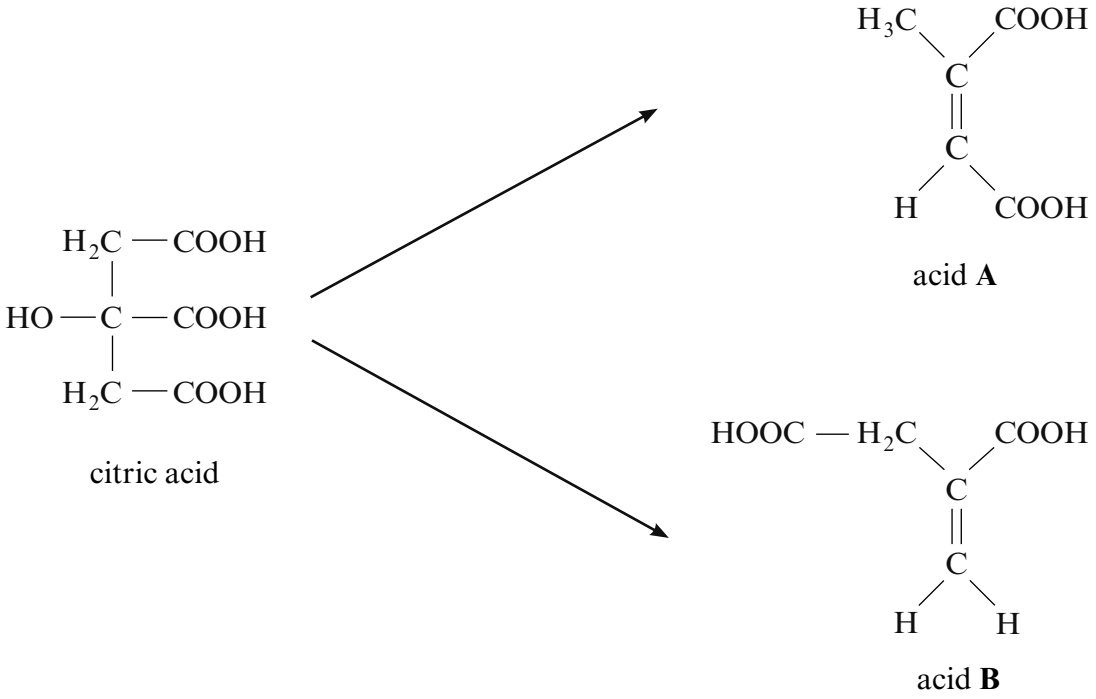
citric acid

This acid has been known since the 8th century and from about 1890 it began to be isolated from citrus fruits. The concentration of citric acid in the juices of these fruits varies from about 0.005 mol dm^{-3} for oranges to 0.300 mol dm^{-3} for lemons. However, most citric acid is now made from sugars by the use of a fungus. After treatment with this material the mixture is filtered and then reacted with calcium hydroxide, to precipitate insoluble calcium citrate. This is then treated with sulfuric acid to produce citric acid and calcium sulfate.

$$\underset{\text{calcium citrate}}{(C_6H_5O_7)_2Ca_3} + 3H_2SO_4 \longrightarrow 2C_6H_8O_7 + 3CaSO_4$$

$M_r = 498$ $M_r = 98$ $M_r = 192$

On heating, citric acid gives two unsaturated acids by the loss of water and subsequent decarboxylation.



citric acid

acid **A**

acid **B**

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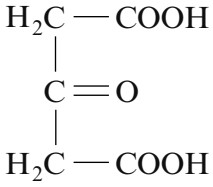
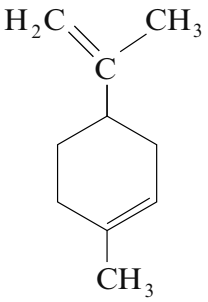
When citric acid is treated with concentrated sulfuric acid, acid **C** is formed.

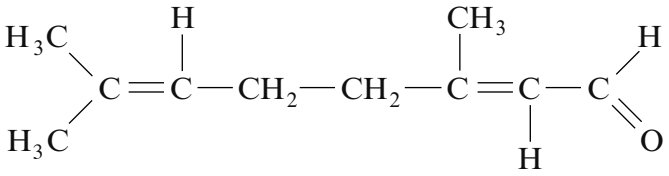


acid **C**

Lemons, from which citric acid was formerly extracted, contain a number of other compounds. Lemon oil is obtained by crushing the peel of lemons. This oil contains about 90% limonene and 5% citral.



limonene



citral

Citric acid remains a very important material today with extensive uses for soft drinks and other important uses in the food and detergent industries.

– End of passage –

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(a) (i) Calculate the atom economy when citric acid is made by the acidification of calcium citrate *(line 10)*. [1]

Atom economy = ... %

(ii) Suggest a way in which this stage of the process could be made more cost effective. [1]

.....

.....

(b) Citric acid occurs in two forms – an anhydrous form and a hydrate.
Some students were given samples of the **hydrated** form of this tribasic acid and were asked to find its relative molecular mass by a titration with aqueous sodium hydroxide, using a suitable indicator to monitor complete neutralisation of the acid.

2.31 g of the hydrated acid was dissolved and made up to 250 cm^3 with distilled water. A 25.00 cm^3 sample of this solution needed 26.40 cm^3 of a sodium hydroxide solution for complete neutralisation.

Calculate the total volume of sodium hydroxide solution needed to neutralise all of the acid and then use the graph opposite to help you calculate the relative molecular mass of the hydrated citric acid. Use your answer to calculate the value of n in hydrated citric acid, $C_6H_8O_7.nH_2O$. You are required to show your working in this calculation. [5]

n =.....

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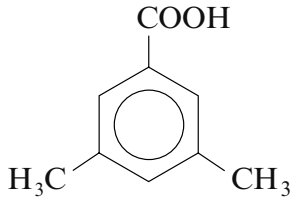
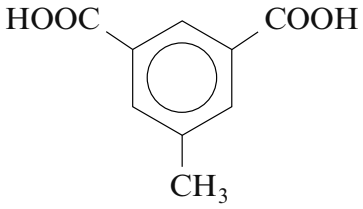
(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



melting temperature 172 °C

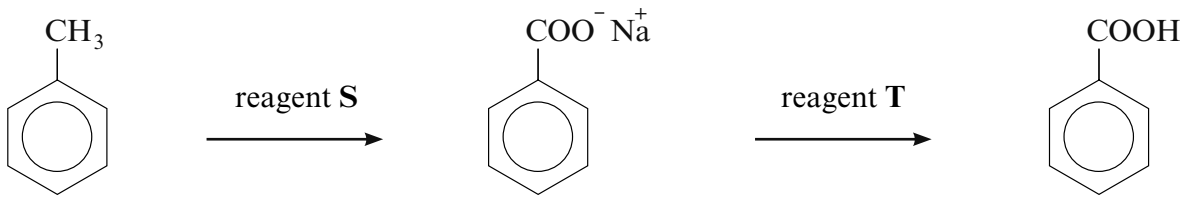
Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water. [4]

(iii) Further oxidation of mesitylene gives 5-methylbenzene-1,3-dicarboxylic acid.



By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol. [1]

(iv) 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]

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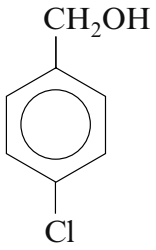
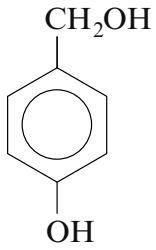
(iii) Explain why the product of the reaction in (ii) is (4-chlorophenyl)methanol and not (4-hydroxyphenyl)methanol. [2]

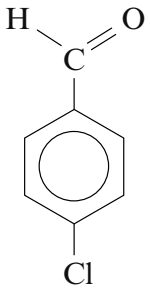


(4-chlorophenyl)methanol



(4-hydroxyphenyl)methanol

(iv) (4-Chlorophenyl)methanol was oxidised to give (4-chlorophenyl)methanal.



The mass spectrum of the product of this reaction showed traces of another compound with molecular ions, m/z, of 156 and 158 in a ratio of 3:1.
Suggest a structural formula for this compound and state why it has these two molecular ions. [2]

Total [20]

Total Section B [40]

END OF PAPER

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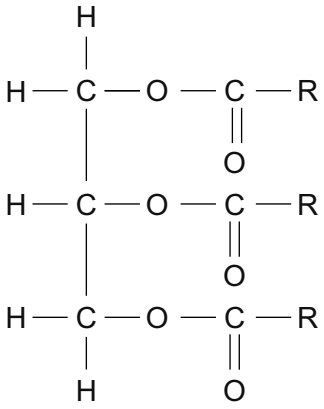
SECTION A

Answer **all** *questions in the spaces provided.*

1. Fats and oils found in living things are esters of fatty acids and glycerol (propan-1,2,3-triol). Fatty acids are carboxylic acids with one —COOH group and a long hydrocarbon chain, often shown as R.

(a) The general structure of a fat is shown below.



The three ester groups in this molecule can be hydrolysed in the same way as other esters. Give the reagent(s) and condition(s) needed for the hydrolysis of this fat, and write a balanced equation for the reaction. [3]

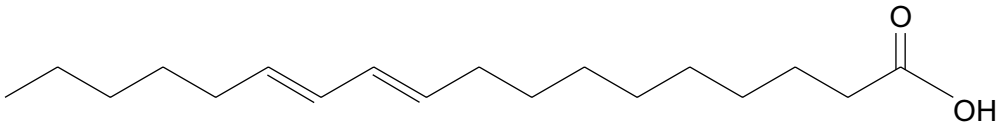
Reagent(s) .....

Condition(s) .....

Equation

Examiner only

(b) One fatty acid is linoleic acid, whose structure is shown below.



(i) This molecule is an unsaturated fatty acid because it contains carbon-carbon double bonds. Give a chemical test to show that a molecule contains carbon-carbon double bonds. [2]

Reagent(s) .....

Observation(s) .....

(ii) Unsaturated fatty acids may be converted into saturated fatty acids by reaction with hydrogen gas in an addition reaction. Give the catalyst required for this reaction. [1]

.....

(iii) The hydrogenation of a sample of linoleic acid to the saturated fatty acid stearic acid (M_r = 284) required exactly 1.15 dm^3 of hydrogen gas for complete reaction. Calculate the maximum mass of stearic acid that could be formed in this reaction. [3]

[1 mol of a gas occupies 24.0 dm^3 at 298K and 1 atm pressure. Assume all gas volumes are measured under these conditions.]

Maximum mass = ... g

QUESTION CONTINUES ON PAGE 4

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(c) Another fatty acid with one carboxylic acid group was found to contain 69.7 % carbon, 11.7 % hydrogen and 18.6 % oxygen by mass.

(i) Calculate the **empirical** formula of this fatty acid. [2]

Empirical formula .....

(ii) Give the **molecular** formula of this fatty acid. [1]

.....

(d) There has been great interest in converting fats and oils into biodiesel as an alternative to fossil fuels produced from crude oil. Give **one** advantage of using biodiesel as an alternative to fossil fuels. [1]

.....

.....

Total [13]

13

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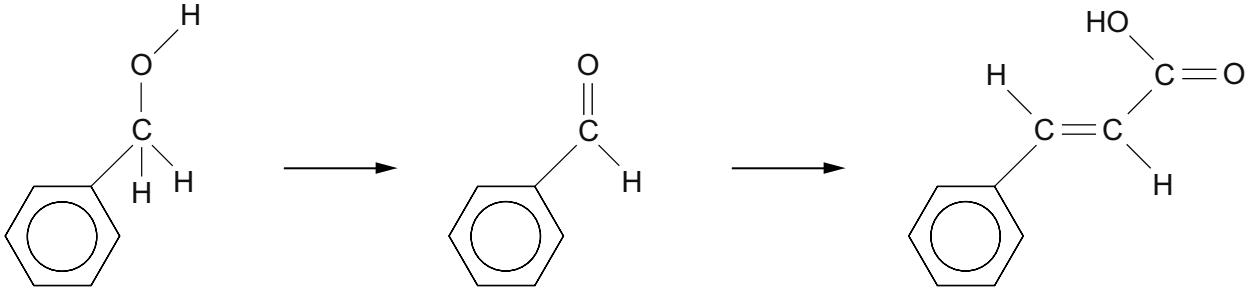
(c) Another compound synthesised by Perkin was cinnamic acid. Cinnamic acid can be produced in two steps from phenylmethanol as shown below.



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]

1094 010007

Mass = ... g

(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]

.....

.....

.....

.....

.....

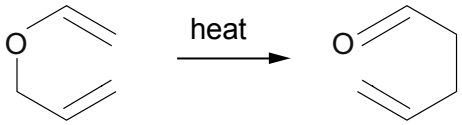
Total [13]

13

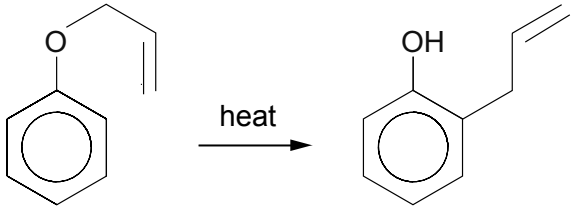
3. *Read the passage below and then answer the questions in the spaces provided.*

Rearrangement reactions

The many different chemical reactions that occur for organic compounds can be classified in different ways, and reaction types such as addition, substitution and elimination are familiar to all students of organic chemistry. A different group of organic reactions is the rearrangement reactions, where the product has the same molecular formula as the starting material. One of the first rearrangement reactions to be identified was the Claisen rearrangement and two examples of this are given below.



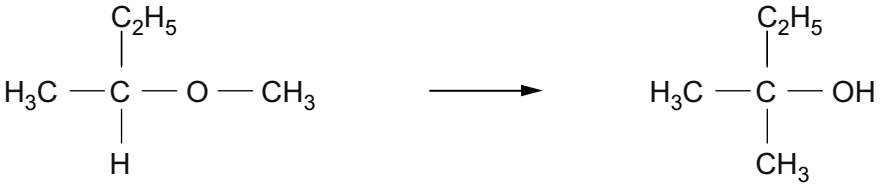
Claisen rearrangement



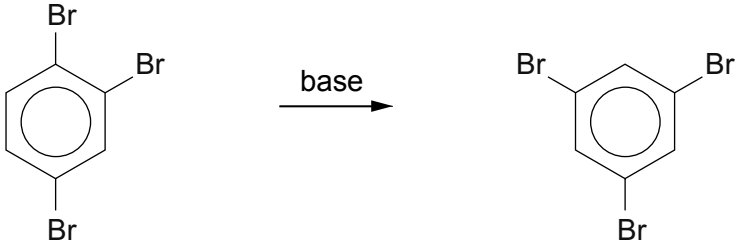
aromatic Claisen rearrangement

This rearrangement can occur in a wide range of molecules, and so it is used in the production of a number of biologically active molecules including *Pancratistatin* and *Halomon*, both of which have antitumour activity. The rates of these reactions are much higher in polar solvents, especially those that can form hydrogen bonds, and the rate can also be increased by using catalysts containing aluminium compounds.

Another group of rearrangement reactions is the 1,2-shift reactions where a side chain or a functional group moves from one atom to an adjacent carbon atom. An example is the 1,2-Wittig rearrangement where an alkoxy compound rearranges to form an alcohol. An alkyl lithium compound is used to initiate the reaction.



1,2-rearrangement reactions can also occur in benzene compounds, and one example is the halogen dance reaction which is shown below.



Rearrangement reactions are of great interest in modern chemistry as they meet the aims of green chemistry and provide an alternative to multistep processes where each part of a molecule is added in turn. They also provide a straightforward route to the formation of carbon-carbon covalent bonds.

– End of passage –

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(d) Many of these rearrangement reactions are useful as they create carbon-carbon covalent bonds *(lines 23-24)*. Another way of forming carbon-carbon covalent bonds is the reaction of hydrogen cyanide, HCN, with a carbonyl compound.

Draw the mechanism of the reaction of ethanal with hydrogen cyanide and classify the mechanism. [4]

Classification of mechanism .....

Total [14]

Total Section A [40]

14

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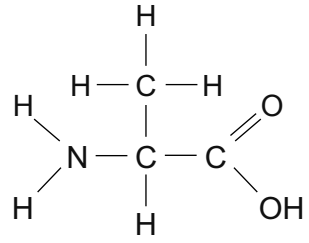
(c) Amino acids contain both — NH_2 and — COOH groups, such as in the molecule below.



alanine *(2-aminopropanoic acid)*

(i) Alanine dissolves in strong acid. Draw the carbon-containing species that would be present in this solution. [1]

(ii) When two molecules of alanine react together they make a dipeptide. Draw the structure of this dipeptide, circling the peptide link. [2]

(iii) Alanine has a melting temperature of 258 °C. This is much higher than compounds with molecules of a similar size such as butanoic acid, which has a melting temperature of −8 °C. Explain why the melting temperatures of these two compounds are so different. [2]

(iv) Alanine can undergo decarboxylation. Give the reagent(s) required for this reaction and identify the organic product formed. [2]

Total [20]

Total Section B [40]

END OF PAPER

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SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* 1-Chloropentane can be made by the free radical chlorination of pentane, in a similar way to the reaction of methane with chlorine.

(i) Give the equation for the reaction of pentane with chlorine, showing the displayed formula of 1-chloropentane as part of your answer. [1]

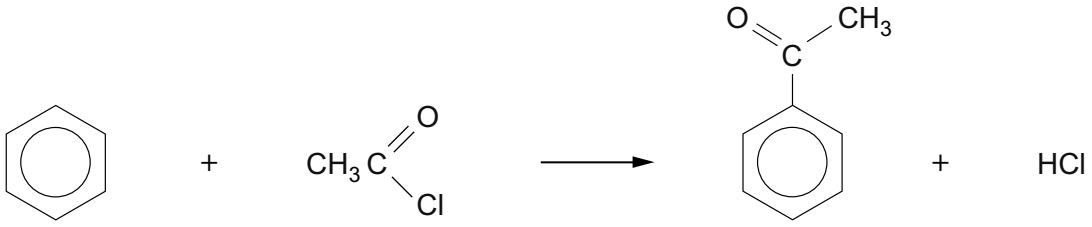
(ii) The free radical reaction of pentane with chlorine gives other chlorinated organic products. Give the structural formula of the carbon-containing free radical that leads to the formation of 2-chloropentane. [1]

.....

(b) Pentylbenzene can be produced by the reaction of 1-chloropentane and benzene in a Friedel-Crafts reaction. State the name of a catalyst that can be used in this reaction. [1]

.....

(c) A Friedel-Crafts reaction can be carried out with ethanoyl chloride in place of 1-chloropentane. This reaction gives phenylethanone as the main organic product.



phenylethanone

(i) State what is seen when a few drops of phenylethanone are added to a solution of 2,4-dinitrophenylhydrazine. [1]

.....

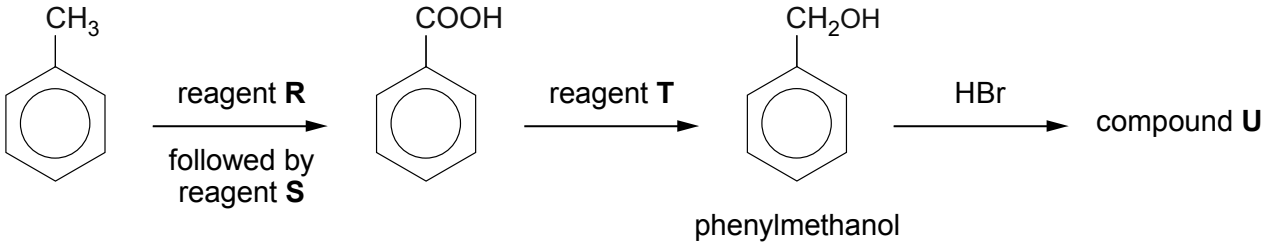
Examiner only

(ii) This preparation of phenylethanone also gives small traces of an impurity. This impurity has a molecular formula $C_{10}H_{10}O_2$ and reacts in a similar way to phenylethanone when it is treated with 2,4-dinitrophenylhydrazine. It does not react with Tollens' reagent. Suggest a displayed formula for this impurity, giving a reason for your choice. [2]

.....

.....

(d) Methylbenzene can be oxidised to benzoic acid by heating it strongly with an alkaline solution of reagent **R** followed by treatment with reagent **S**. The benzoic acid can then be used to produce a number of other compounds. A reaction sequence is shown below.



(i) State the name of reagent **R**. ..... [1]

(ii) State the name of reagent **S**. ..... [1]

(iii) State the name of reagent **T**. ..... [1]

(iv) Give the displayed formula of the organic compound **U**. [1]

(e) State and explain how the infrared spectrum of benzoic acid would differ from that of phenylmethanol. [2]

.....

.....

.....

Total [12]

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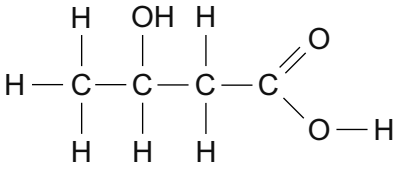
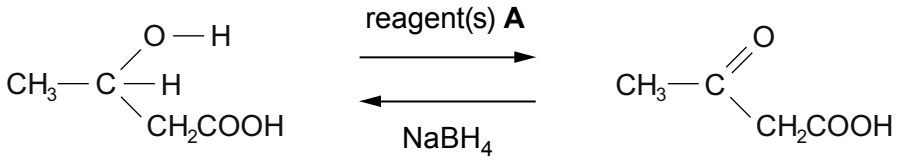
2. 3-Hydroxybutanoic acid is a white solid that can react as a carboxylic acid and an alcohol.

(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), $NaBH_4$.



3-oxobutanoic acid

(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]

.....

.....

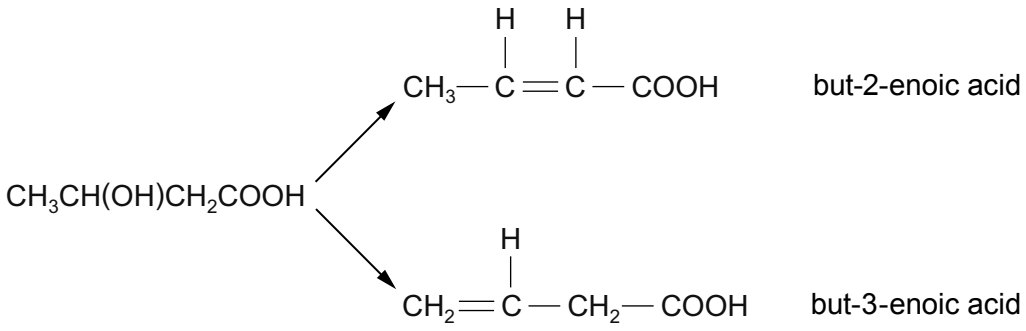
II State the effect (if any) that a racemic mixture has on the plane of polarised light. [1]

.....

.....

Examiner only

(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 .....

1094 010005

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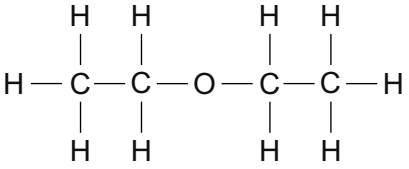
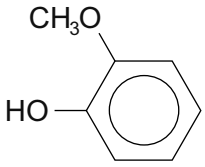
3. *Read the passage below and then answer the questions in the spaces provided.*

The chemistry of some compounds containing the ether (R–O–R) linkage

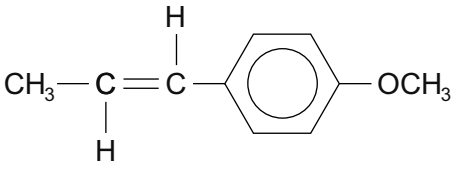
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



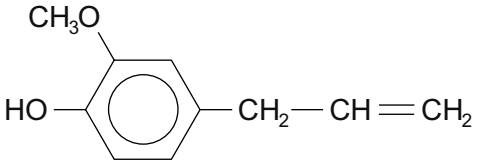
ethoxyethane



guaiacol

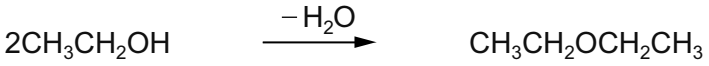


anethole

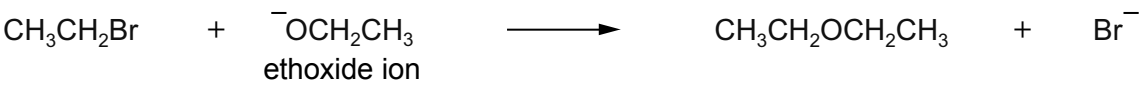


eugenol

Ethoxyethane (diethyl ether) is one of the most familiar compounds containing the ether linkage. It can be made by heating ethanol with an excess of concentrated sulfuric acid, which acts as a dehydrating agent.



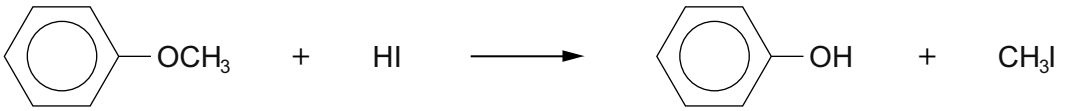
Another method is by reacting bromoethane with sodium ethoxide (a source of the ethoxide ion).



ethoxide ion

Ethoxyethane has a boiling temperature of 35 °C whereas ethanol, a smaller molecule, boils at 78 °C. The solubility of these two compounds in water also varies. Ethanol is completely miscible with water but ethoxyethane has a much reduced solubility.

The strong C—O bond means that compounds such as ethoxyethane and methoxybenzene have relatively few reactions. However, carbon–oxygen bond fission occurs when they are heated with concentrated hydrobromic (HBr) or hydriodic acid (HI).



methoxybenzene

Examiner only

20 Naturally occurring compounds that contain the ether linkage often owe their reactions to other functional groups present in the molecule. Both eugenol (found in cloves) and guaiacol (from wood) have medicinal uses. Anethole (occurring in aniseed) has a promising use as an insecticide and is also effective against some bacteria and fungi.

- End of passage -

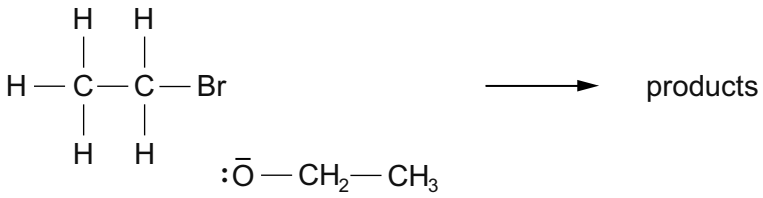
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol (M_r = 46) and obtained a 45 % yield of ethoxyethane (M_r = 74). Calculate the mass of ethoxyethane obtained. [3]

Mass = ... g

(ii) One of the reasons for only obtaining a 45 % yield of ethoxyethane was that sulfuric acid reacted with ethanol in a different reaction. State the organic product of this side reaction. [1]

.....

(iii) Bethan would have obtained a higher percentage yield of ethoxyethane if she had reacted bromoethane with sodium ethoxide *(line 10).* This reaction is an example of nucleophilic substitution. Complete the mechanism below by inserting curly arrows and appropriate partial charges (δ+, δ-). [2]



(iv) Ethoxyethane has a much lower boiling temperature than ethanol because its molecules are unable to hydrogen bond with each other. State the feature of a molecule that needs to be present for hydrogen bonding to occur. [1]

.....

.....

Examiner only

(b) Guaiacol *(line 4)* reacts with (aqueous) bromine.

(i) By analogy with the reaction of phenol with (aqueous) bromine, suggest a displayed formula for the organic product of the reaction between guaiacol and (aqueous) bromine. [1]

(ii) Describe what is seen during this reaction. [1]

.....

(c) The article shows the formulae of anethole and eugenol *(line 5)*. State a reagent that will react with eugenol but not with anethole, giving the observation. [2]

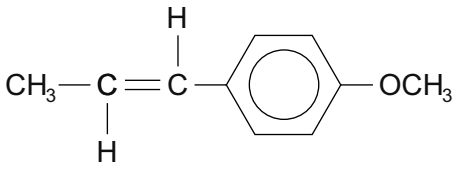
Reagent .....

Observation .....

(d) (i) State the molecular formula of anethole *(line 5)*. [1]

.....

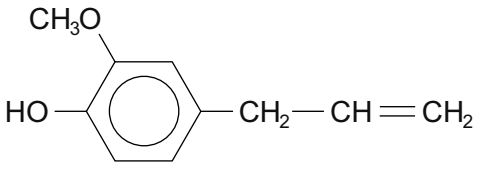
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



anethole

displayed formula of product

(e) An isomer of eugenol *(line 5)*, compound **Y**, reacts with sodium carbonate giving carbon dioxide. Suggest a displayed formula for compound **Y** and state the name of the functional group present in the organic compound that produces carbon dioxide in this reaction. [2]



eugenol

displayed formula for compound **Y**

Functional group .....

Total [15]

Total Section A [40]

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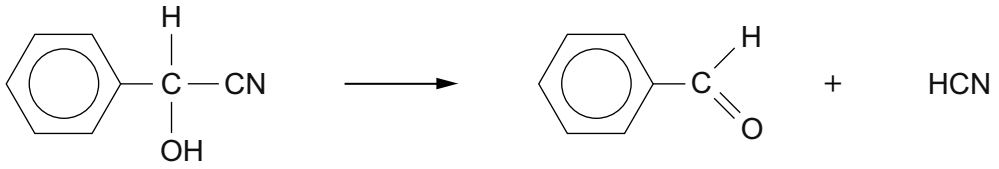
(b) A species of millipede can protect itself by producing hydrogen cyanide. This poisonous gas is produced from mandelonitrile by enzyme action.



2-phenyl-2-hydroxyethanenitrile (mandelonitrile)

benzaldehyde

The reaction can be carried out in the reverse direction in the laboratory.

(i) Draw the mechanism for the reaction between benzaldehyde and the cyanide ion. State the type of mechanism occurring. [4]

(ii) Mandelonitrile is a yellow material. State the general name for groups that cause colour in organic compounds and give the appearance of mandelonitrile when viewed under blue light, giving a reason for your answer. [3]

(iii) Give the structural formula of the organic compound obtained when mandelonitrile is warmed with dilute hydrochloric or sulfuric acid. [1]

Total [20]

TURN OVER FOR QUESTION 5

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