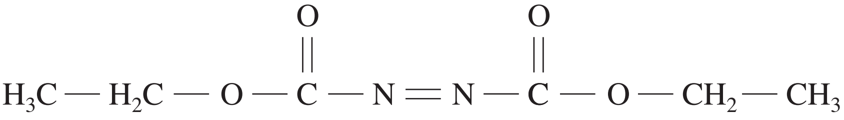
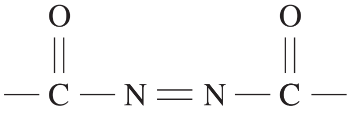
(c) Diethyl azodicarboxylate (abbreviated to DEAD)



$$H_3C-H_2C-O-\overset{\overset{\displaystyle O}{\|}}{C}-N=N-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3$$

is a shock-sensitive, toxic orange liquid.

(i) The conjugated system shown below is present in DEAD and is described as a chromophore.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-N=N-\overset{\overset{\displaystyle O}{\|}}{C}-$$

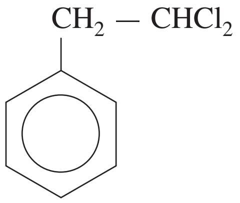
I. State the meaning of the term chromophore. [1]

II. Explain why DEAD is an **orange** liquid. [1]

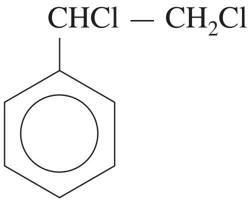
(ii) The NMR spectrum of DEAD shows two series of peaks – a quartet and a triplet. Explain how the splitting of these peaks arises. [2]

Total [13]

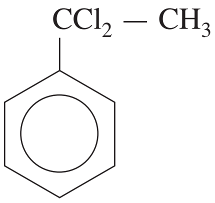
(b) (2-Chloroethyl)benzene can be made by reacting ethylbenzene with chlorine. During this reaction a number of other compounds, including the following, are produced.



compound **R**

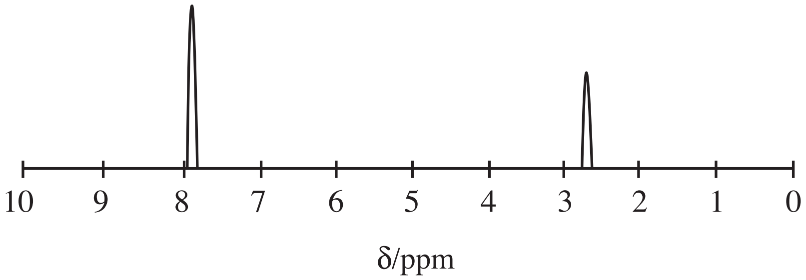


compound **S**



compound **T**

The low resolution NMR spectrum of one of these compounds is shown below.



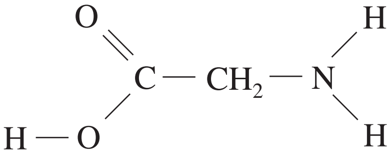
State, giving a reason, which of the three compounds **R**, **S** or **T** will have the low resolution NMR spectrum shown. [2]

....

....

....

(c) (i) Aminoethanoic acid (glycine), whose displayed formula is shown below, reacts with ethanoyl chloride.



Give the equation for this reaction, showing the displayed formula of the organic product. [2]

....

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.

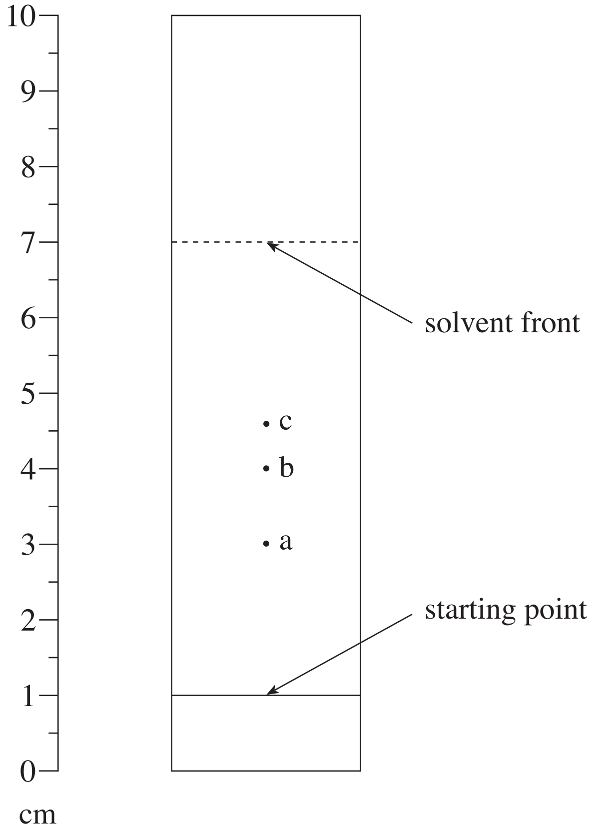
One industrial method for the production of ethanoic acid is to react methanol and carbon monoxide at a temperature of 450 K and a pressure of 30 atmospheres, in the presence of a suitable catalyst. The methanol and carbon monoxide have to be produced from coal, oil or natural gas. The process gives 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 used to make bottles and in textiles such as *terylene*, whereas polyvinyl acetate (PVA) is used as an adhesive. 25

- End of passage -

(d) The passage shows a TLC chromatogram of a mixture of three ethyl esters of different carboxylic acids.
The retardation factor (R_f value) of ethyl palmitate (hexadecanoate) is 0.60.
Use the chromatogram to decide which of the three spots, if any, is given by ethyl palmitate, showing how you arrived at your answer. [2]

....

....

....

....

(e) The polymer PET *(line 24)* is made from ethane-1,2-diol and benzene-1,4-dicarboxylic acid.
Give the formula of a section of this polymer, identifying the repeating unit. [2]

Total [15]

Section A Total [40]

(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.

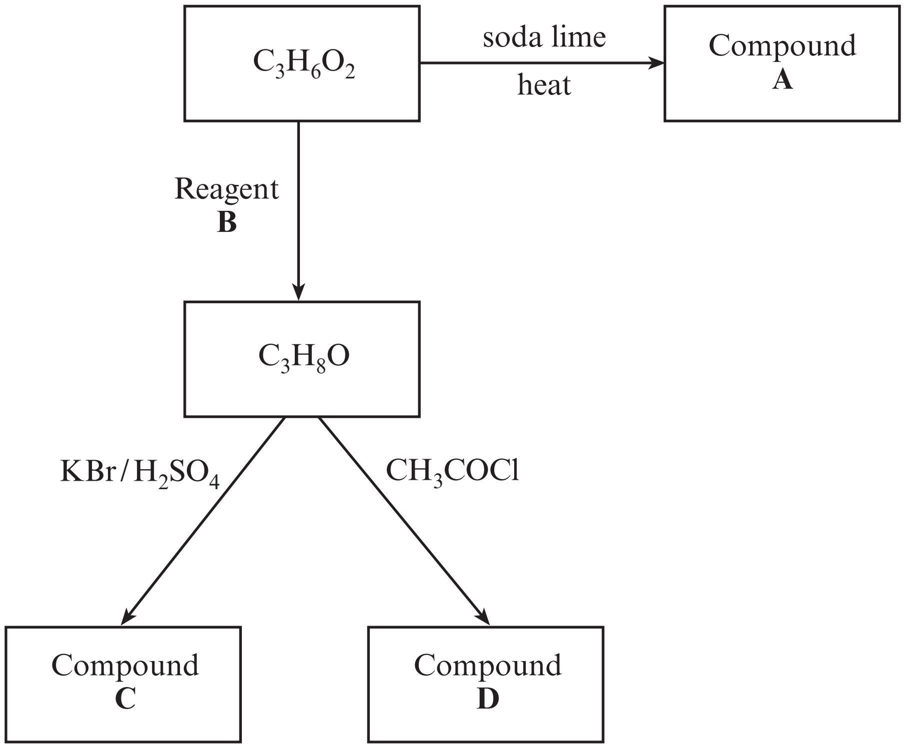
You should assume that any compound produced has been separated and purified. [3]

(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]

(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]

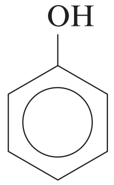
....

Total [10]

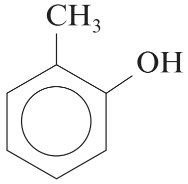
3. *Read the passage below and then answer the questions in the spaces provided.*

Phenol

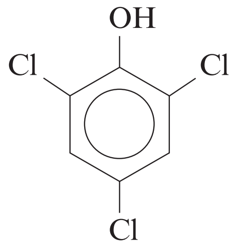
Phenol, formula C_6H_5OH, has an hydroxyl group joined directly to an aromatic ring.



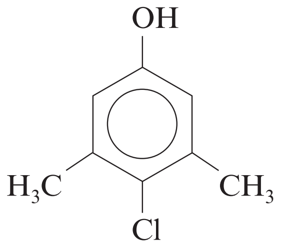
Phenol has many derivatives including 2-methylphenol.



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 –

(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]

....

....

....

....

(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]

SECTION B

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

4. *(a)* The reaction between but-1-ene and hydrogen bromide produces a mixture of **three** isomers.

(i) Draw the displayed formula of each of the three isomers. [3]

(ii) Outline how each of the isomers can be distinguished from one another. [3]

(QWC) [1]

(b) (i) Ethylamine can be produced by the reaction of ammonia with chloroethane.

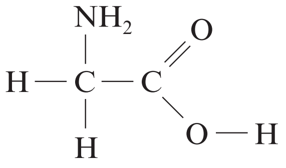
I. Write an equation for this reaction. [1]

II. Classify the type of reaction taking place. [1]

(ii) Phenylamine cannot be prepared in this way. Name the starting material and reagent(s) used to prepare phenylamine in a laboratory. [2]

(iii) Give one chemical test, including reagent(s), condition(s) and expected observations, which would distinguish between ethylamine and phenylamine. [3]

(c) Amino acids also contain an amine group. The simplest amino acid, aminoethanoic acid (glycine) has the formula



(i) Draw the displayed formula of 2-aminopropanoic acid (alanine). [1]

(ii) A dipeptide can be formed by reacting two amino acids. Draw the displayed formulae of the two different dipeptides which can be made by combining glycine and alanine. [2]

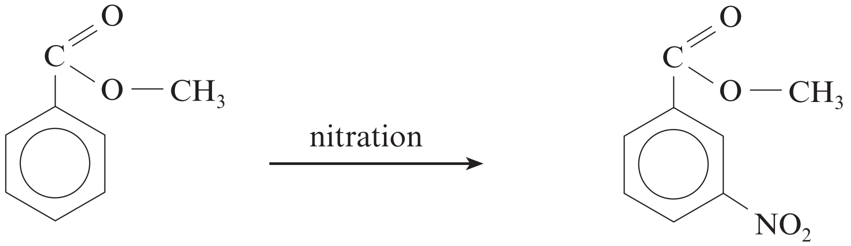
(iii) Proteins are natural polypeptides. Explain briefly what is meant by primary, secondary and tertiary protein structure. [3]

Total [20]

5. *(a)* Describe the structure of, and bonding in, benzene and explain why benzene is less ready to undergo addition reactions than alkenes. [6]

(QWC) [2]

(b) Frances wanted to prepare a nitro-aromatic compound in the laboratory, so her teacher told her to prepare methyl-3-nitrobenzoate by nitrating methyl benzoate using the following method.



methyl benzoate methyl-3-nitrobenzoate

- Prepare a nitrating mixture by mixing 2 cm^3 of concentrated nitric acid and 2 cm^3 of concentrated sulfuric acid in a test tube, cooling it in ice.
- Weigh 2.75 g of methyl benzoate in a small conical flask, place the flask in a beaker of ice and slowly add 5 cm^3 of concentrated sulfuric acid.
- Add the nitrating mixture a few drops at a time to the solution in the flask ensuring that the temperature stays below 10 °C.
- When the addition is complete, allow the mixture to stand at room temperature for 15 minutes.
- Pour the mixture onto crushed ice in a small beaker, stir and leave until all the ice has melted and crystals have formed.
- Filter the mixture, wash well with water and recrystallise it from ethanol.

At the end of the experiment Frances' yield was 2.70 g.

(i) Suggest why the teacher told her to nitrate methyl benzoate, not benzene. [1]

(ii) State why it is necessary to recrystallise the product before weighing it. [1]

(iii) Outline how Frances would recrystallise methyl-3-nitrobenzoate from ethanol. [3]

(iv) State how she could prove that the product was pure. [1]

(v) Methyl benzoate is a liquid at room temperature and has a density of 1.1 g cm^{-3}. Calculate the volume of 2.75 g of methyl benzoate. [1]

(vi) Calculate the percentage yield obtained by Frances. [3]

(vii) Methyl benzoate undergoes nitration by the same mechanism as benzene.

I. Classify the mechanism for the nitration of methyl benzoate. [1]

II. Give the formula of the species attacking the benzene ring. [1]

Total [20]

Section B Total [40]

SECTION A

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

1. *(a)* Complete the following passage by inserting suitable words or formulae where required. [3]

Nitrobenzene, an aromatic yellow oil, has the molecular formula ....

However, in blue light, this compound appears black because ....

....

The ^{1}H NMR spectrum of nitrobenzene is produced as a result of interactions between the spin of the nuclei and an applied magnetic field. This spectrum is seen as a number of peaks because the protons causing the spectrum are not ....

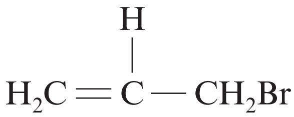
(b) Benzene reacts with chloromethane in the presence of a catalyst giving methylbenzene as the main organic product.

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

(ii) State the name of a catalyst that can be used. [1]

....

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

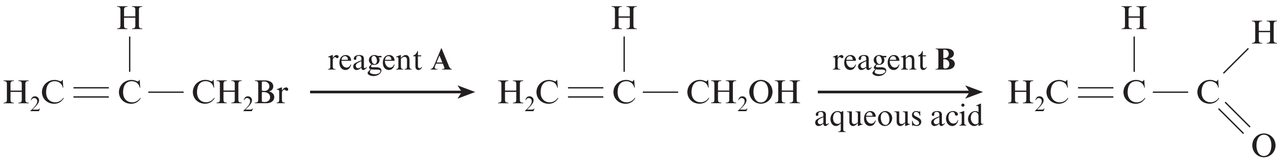


$$\mathrm{H_2C{=}\overset{H}{\overset{|}{C}}{-}CH_2Br}$$

(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 $\mathrm{cm^{-1}}$ and at 2500-3550 $\mathrm{cm^{-1}}$.
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 ....

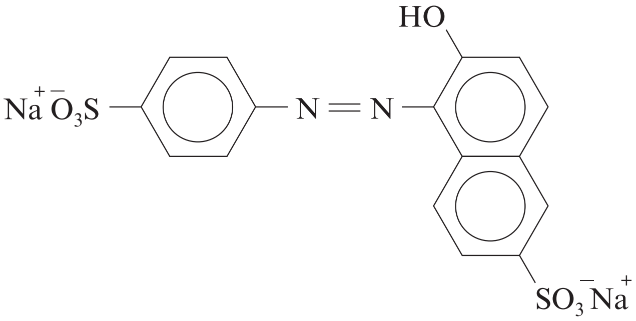
Type of reaction ....

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

Food additives

Since 1986 manufacturers have been required, for most foods, to list their ingredients in descending proportions by mass. Food additives can be listed by their chemical names or by using an E-number. They are used for a number of reasons and as a result they are classified into different groups, some of which are discussed in this article.

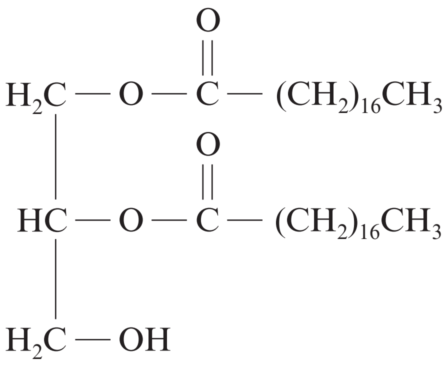
Colouring agents Consumers are probably most worried about compounds used to colour food. A number of permitted colours are synthetic azo-dyes and there are particular concerns about the effect that some of these compounds have on children. In recent years there has been a move towards safer naturally occurring dyes such as annatto and anthocyanins.
However, azo-dyes such as Sunset Yellow FF (E110) continue to be used.



E110

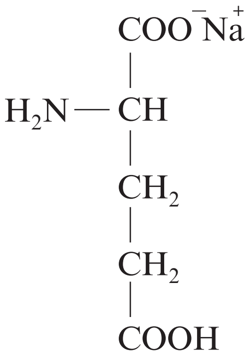
Preservatives With the move towards foods having longer shelf lives, there is a need to use preservatives to prevent spoilage. 2-Hydroxypropanoic acid (lactic acid), occurs naturally in sour milk and is used as a preservative in salad dressings. The salts of organic acids, for example sodium benzoate and sodium citrate, are used in fizzy drinks.
Calcium propanoate, $(CH_3CH_2COO)_2Ca$, is used as a preservative in bread, as it inhibits the growth of mould-producing microorganisms.

Emulsifiers These are used to enable oily substances and water to mix, so that separation into two layers does not occur. These compounds generally have water-‘soluble’ groups and a hydrocarbon chain that is fat-‘soluble’. An example is the ester E477.



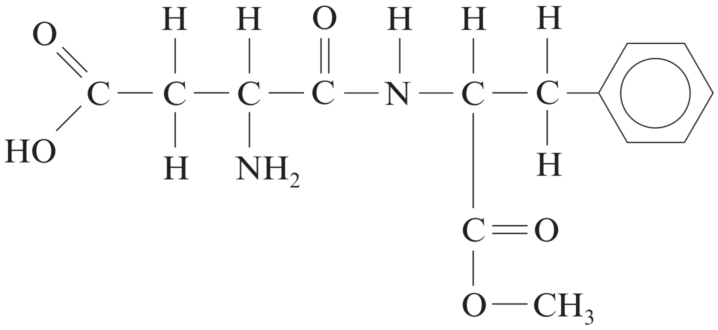
E477

Flavour enhancers Compounds such as monosodium glutamate (MSG) are added to food to increase its flavour. MSG occurs naturally in Parmesan cheese and tomatoes. Perhaps that is the reason why pizzas and soups are sometimes garnished with cheese and tomato.



MSG

Artificial sweeteners Many consumers are suspicious of food that has added sugar and manufacturers are naturally keen to label their products as containing ‘no added sugar’. This may be true, but very often artificial sweetening agents are added in place of sugar to make the food more palatable. One of the commonest of these is aspartame, which is 200 times sweeter than sugar.



aspartame

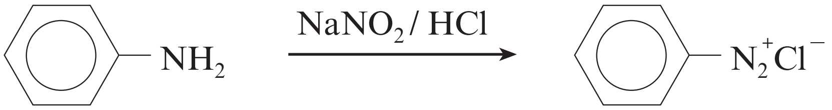
The use (and misuse) of additives is an area of chemistry that has increasing importance as world population increases leading to a greater reliance on prepared, rather than fresh food.

– End of passage –

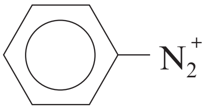
(a) (i) State the general name given to groups present in compounds such as Sunset Yellow FF that gives them their colour. [1]

(ii) Sunset Yellow FF is soluble in water. Like sodium chloride it contains sodium ions, Na^+. Explain how sodium ions interact with water molecules. [1]

(iii) In the first stage of preparing an azo-dye, an aromatic amine reacts with sodium nitrate(III) (nitrite) and hydrochloric acid to give a diazonium compound.

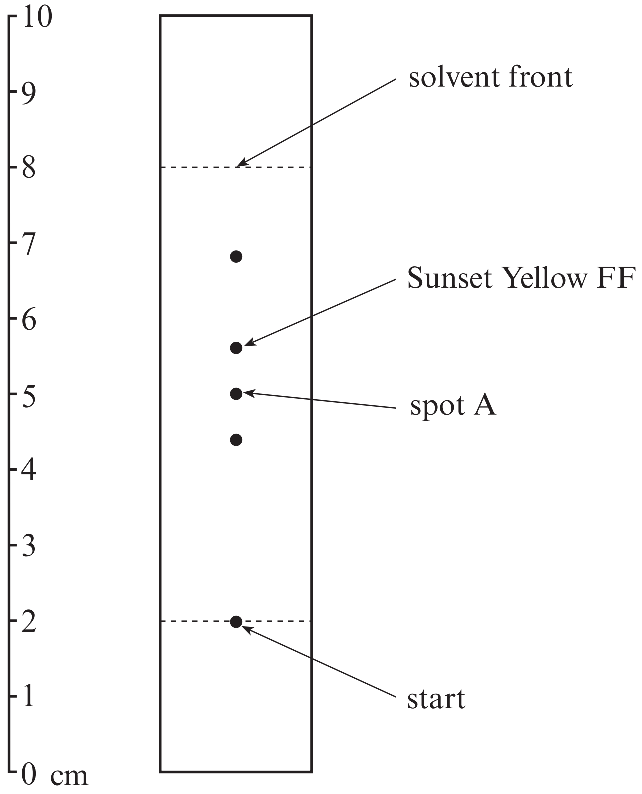


I. State the temperature required for this reaction. [1]

II. The benzenediazonium ion,  , then reacts with a phenol to produce an azo-dye.

The benzenediazonium ion reacts as an electrophile.
State what is meant by the term *electrophile*. [1]

(b) A government chemist was using thin layer chromatography to identify the colours found in some imported sweets. She obtained the chromatogram below.



The R_f values for some of the expected colours are given in the following table.

Colour	R_f value
Sunset Yellow FF	0.60
Brilliant Blue FF	0.80
Fast Green FF	0.90

(i) Use the table of R_f values to state which other colour, apart from Sunset Yellow FF, is definitely present. Use the chromatogram to show how you arrived at your answer. [2]

....

....

(ii) The chemist suspected that spot A was due to amaranth or indigo carmine.
This spot was removed from the plate and dissolved in a suitable solvent.
Suggest **two** methods that she could then use to decide which of these two dyes was present. [2]

1. ....

....

2. ....

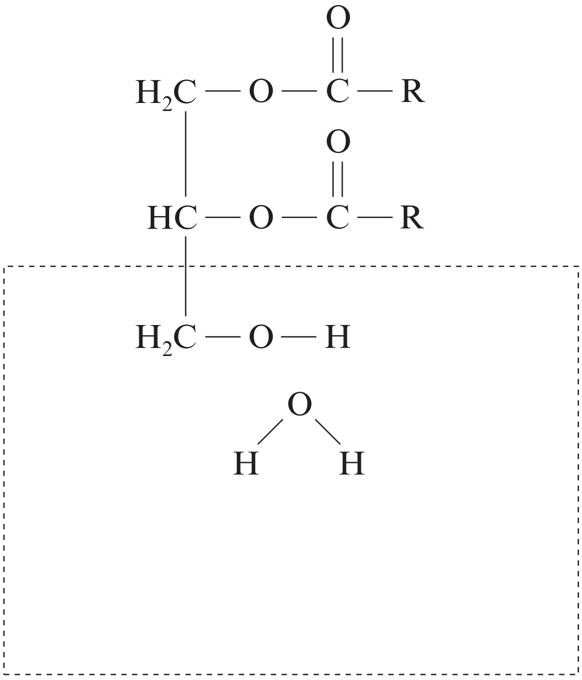
....

(c) Calcium propanoate *(line 14)* is used to inhibit mould growth in bread.
Salts of carboxylic acids, such as calcium propanoate, undergo decarboxylation when heated with calcium hydroxide or sodalime.
Complete the equation by giving the formula of the only organic product and balance the equation. [2]

$(CH_3CH_2COO)_2Ca \quad + \quad Ca(OH)_2 \quad \rightarrow \quad \boxed{}\, CaCO_3 \quad + \quad \boxed{}$ ……………………………………

(d) E477 *(line 18)* forms hydrogen bonds with water molecules.

Working inside the box only, complete the diagram below by showing the polarity in E477 and the water molecule and the hydrogen bonds between them. For simplicity the hydrocarbon chain in E477 is shown as R. [2]



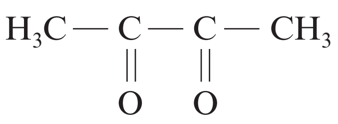
(b) (i) Yoghurt contains lactic acid that has been produced from lactose by certain bacteria.
The percentage of lactic acid in yoghurt can be found by an acid-base titration.
A sample of plain yoghurt of mass 50.0 g was titrated with sodium hydroxide solution of concentration 0.250 mol dm^{-3}. The lactic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

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

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

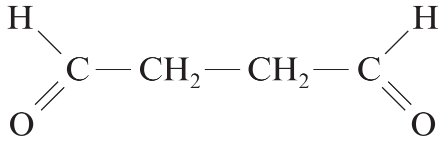
(ii) Some students suggested that it would be less wasteful if just a 10 g sample of yoghurt was used, rather than a 50 g sample, in this titration.
Explain why this would be likely to give a less accurate result. [1]

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



$H_3C-\underset{\underset{O}{||}}{C}-\underset{\underset{O}{||}}{C}-CH_3$

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 ^{1}H 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]

SECTION A

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

1. *(a)* Nitrobenzene, $C_6H_5NO_2$, is a yellow oily liquid.

(i) Give the general name of a group responsible for colour in organic compounds. [1]

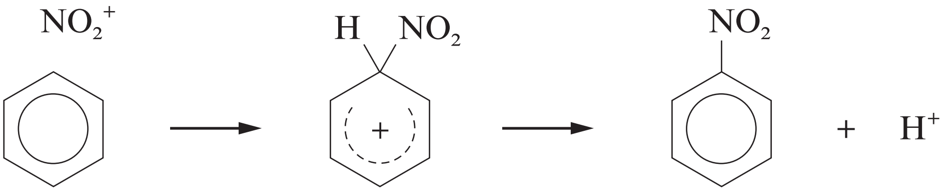
....

(ii) State why nitrobenzene is yellow in white light. [1]

....

(b) Nitrobenzene is produced from benzene by reaction with the nitronium ion (nitryl cation), NO_2^+.

(i) Complete the mechanism below by the use of the curly arrows (↷) [1]



(ii) During this reaction to produce nitrobenzene small quantities of 1,3-dinitrobenzene are produced.
Give the **empirical** formula of 1,3-dinitrobenzene. [1]

....

(iii) In this reaction the nitronium ion is produced from nitric and sulfuric acids.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Use this equation to state why the sulfuric acid is acting as an acid. [1]

....

....

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]

....

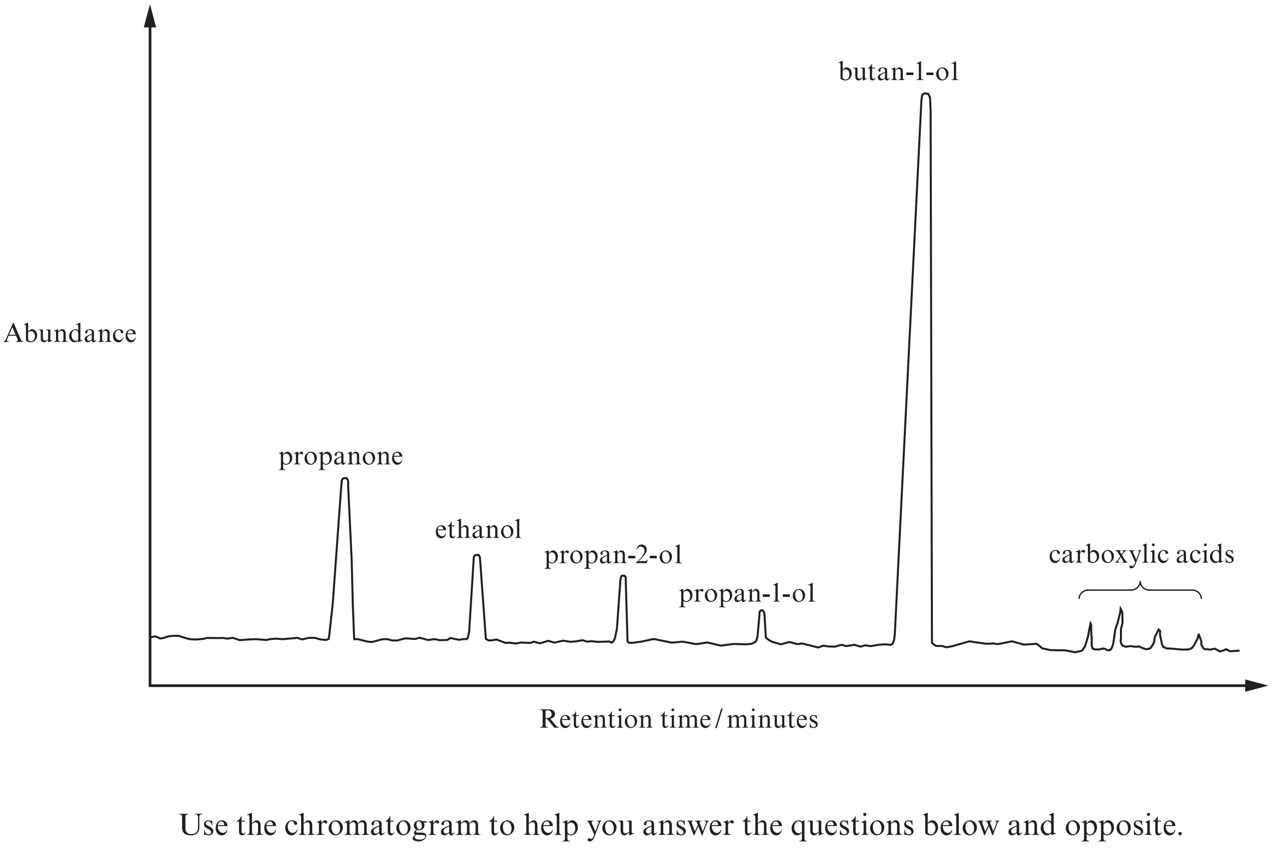
(ii) The infrared spectrum of butanal shows an absorption at 1731 cm^{-1}.
State which bond in butanal is responsible for this absorption and explain how the intensity of this absorption changes as the reduction proceeds. [2]

....

....

....

(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]

....

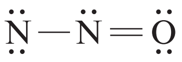
Read the passage below and then answer parts (a)-(g) in the spaces provided.

3.

Anaesthetics

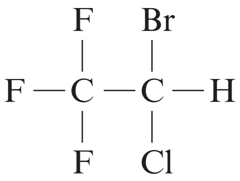
It is difficult to believe, in these days of modern medicine, that only 100 years ago tooth extractions were still being carried out without any form of anaesthetic. Modern anaesthetics are of two types – general anaesthetics, which have a whole body effect and local anaesthetics, which remove pain at the site of surgery.

The first demonstrations of anaesthesia were in the late 1840s when Morton, in the USA, used ethoxyethane, and Simpson, in Scotland, used chloroform (trichloromethane). Later that century nitrous oxide, N_2O, was successfully used. In more recent times, up to about 1960, the most commonly used anaesthetics were cyclopropane and ethoxyethane. In the 21st century a number of safer general anaesthetics are in use, the choice depending on the condition for which they are being used. The formulae of some general anaesthetics are show below, together with their common names.



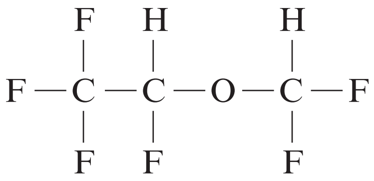
$\underset{\cdot\cdot}{\ddot{N}}-\ddot{N}=\underset{\cdot\cdot}{\ddot{O}}$

nitrous oxide



$$\begin{array}{ccccccc} & & F & & Br & & \\ & & | & & | & & \\ F & - & C & - & C & - & H \\ & & | & & | & & \\ & & F & & Cl & & \end{array}$$

halothane

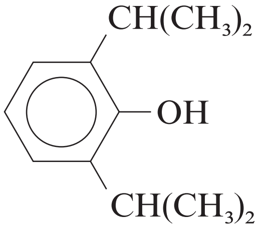


$$\begin{array}{ccccccccccc} & & F & & H & & & & H & & \\ & & | & & | & & & & | & & \\ F & - & C & - & C & - & O & - & C & - & F \\ & & | & & | & & & & | & & \\ & & F & & F & & & & F & & \end{array}$$

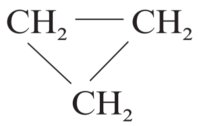
desflurane

$CH_3CH_2OCH_2CH_3$

ethoxyethane

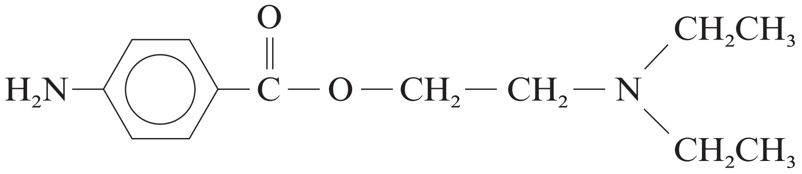


propofol

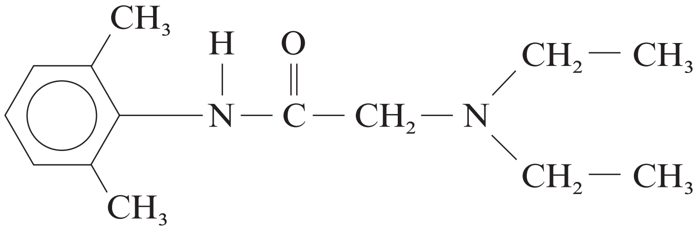


cyclopropane

In the twentieth century, the general anaesthetic nitrous oxide was still being used for routine dental extractions but in recent years the use of local anaesthetics has become the norm. A popular choice for dentists is the ester procaine, although a number of other compounds are available; their use depending on the anaesthetic effect required and its duration of action. The formulae and common names of some local anaesthetics are shown below.

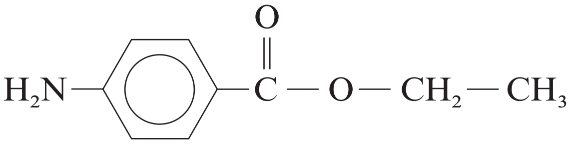


procaine



xylocaine

Benzocaine, for external use only, has uses in skin creams for which a numbing action is required.



benzocaine

The relative safety of the anaesthetic itself is an important factor in deciding which anaesthetic to use for each situation. However, another factor to be considered is the method by which the body metabolises the anaesthetic and the nature of the compounds that are produced.

– End of passage –

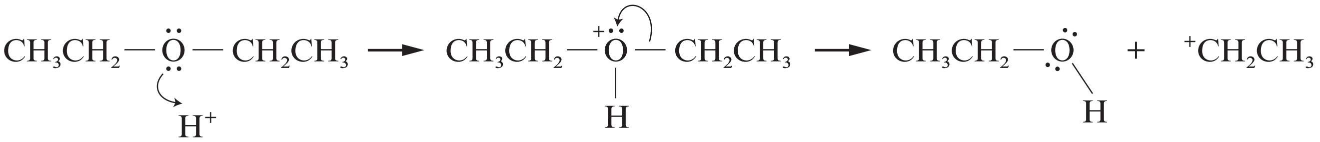
(a) In the upper atmosphere nitrous oxide (dinitrogen oxide), N_2O, decomposes to nitrogen and nitrogen monoxide.

$$2N_2O \longrightarrow N_2 + 2NO$$

Nitrogen monoxide is a reactive molecule that contains an unpaired electron.
State the general name for species that contain an unpaired electron. [1]

(b) The use of cyclopropane as an anaesthetic causes concern because of its extreme flammability. Give the balanced equation for the complete combustion of cyclopropane, C_3H_6. [1]

(c) Ethoxyethane, $CH_3CH_2OCH_2CH_3$, reacts with some aqueous acids to give ethanol as one of the products.
One stage of this reaction can be represented as follows:



(i) State why ethoxyethane is behaving as a nucleophile in this reaction stage. [1]

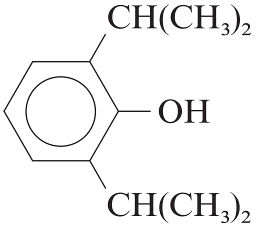
(ii) I To reduce the danger of fire when carrying out this reaction, the reactants are heated together under reflux.
State what is meant by the term *heating under reflux*. [1]

II The reactants need to be refluxed at a temperature of 130 °C.
Suggest how this mixture could be safely heated at this temperature in a laboratory fume cupboard. [1]

(d) The article mentions the use of halothane *(line 12)* and desflurane *(line 12)* as general anaesthetics. State and explain which of these two compounds could cause more damage to the ozone layer. [2]

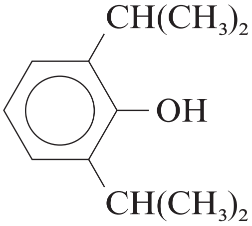
(e) Propofol, which allegedly caused the death of Michael Jackson in 2009, is an important intravenous anaesthetic.

(i) State what would be seen if a few drops of iron(III) chloride solution were added to a solution of propofol in a suitable solvent. [1]

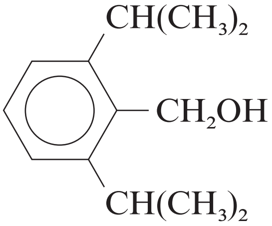


propofol

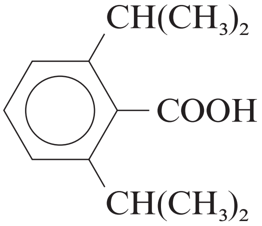
(ii) The formulae of propofol, compound **L** and compound **M** are shown below.



propofol



compound **L**



compound **M**

I The three compounds are dissolved separately in a suitable solvent and each solution tested with universal indicator paper and with sodium hydrogencarbonate solution. Complete the table below giving any **observations** or writing 'no reaction' as appropriate.

Compound	Colour given with universal indicator paper	Observation with sodium hydrogencarbonate solution
propofol		
compound **L**	green	no reaction
compound **M**		

[2]

II Give the test for any gas produced with sodium hydrogencarbonate solution. [1]

(f) The article describes procaine *(line 19)* as an ester.

(i) Draw the section of the formula that identifies procaine as an ester. [1]

(ii) Use the formula of procaine to help you draw the structural formula of the nitrogen-containing alcohol that will react with a suitable acid to give procaine. [1]

(g) Pure benzocaine has a melting temperature of 89°C. A melting temperature determination shows that a sample of benzocaine is impure.
State **two** observations that would indicate that this sample is impure. [2]

....

....

....

Total [15]

Total Section A [40]

(iii) The mass spectrum of DMF, $C_6H_8O_4$, shows only a weak signal for its molecular ion at m/z 144. The strongest signal is seen at m/z 113. Suggest a molecular formula for the positive ion at m/z 113, giving your reasoning. [2]

(b) Fumaric acid (*E*-butenedioic acid) is an important starting compound for the manufacture of many other materials. The usual method for producing fumaric acid is from crude oil, but there is increasing interest in a fermentation route, using enzymes, from a sugar such as glucose. A comparison of these two methods is shown in the table.

	Crude oil route	Fermentation route
Raw material	Maleic anhydride	Glucose
Reaction temperature / °C	95	35
Raw material price / £ kg^{-1}	1.00	0.30

(i) Suggest **one** way that the crude oil route could be made more economic to operate. [1]

(ii) At present the crude oil route is the more economic route from which to obtain fumaric acid.
Suggest **one** factor by which the fermentation route could be modified to make it more competitive with the crude oil route, other than by simply increasing the yield. You are reminded that the optimum temperature for enzymes in this reaction is 35 °C. [1]

(iii) Fumaric acid was obtained in a pilot-scale experiment by the fermentation route, using glucose.
A simplified equation for the reaction is shown below.

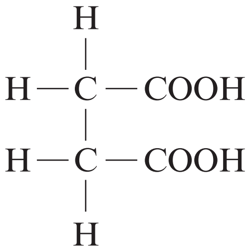
$$2CO_2 + \underset{M_r\,180}{C_6H_{12}O_6} \longrightarrow \underset{M_r\,116}{2C_4H_4O_4} + 2H_2O$$

In this experiment 12.6 kg of glucose (70 moles) gave 13.0 kg of fumaric acid. Calculate the percentage yield of fumaric acid. [3]

(iv) Small amounts of other organic acids are produced during the fermentation.

I One of these acids is ethanoic acid.
Outline any **one** other reaction that produces ethanoic acid.
Your answer should include
- the name of your starting material,
- any other reagent(s) used,
- the type of reaction occurring. [3]

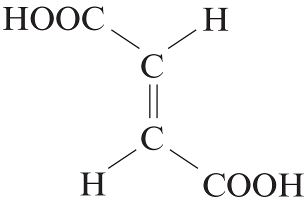
II A small amount of butanedioic acid is also produced.



$$\begin{array}{l}\quad\;\mathrm{H}\\\quad\;|\\\mathrm{H-C-COOH}\\\quad\;|\\\mathrm{H-C-COOH}\\\quad\;|\\\quad\;\mathrm{H}\end{array}$$

butanedioic acid

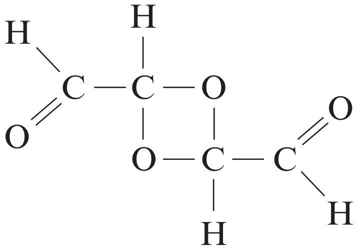
This acid can also be produced by the hydrogenation of the unsaturated acid, fumaric acid.



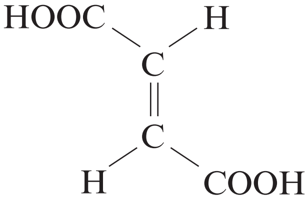
fumaric acid

Suggest a suitable catalyst for this hydrogenation. [1]

(c) A research student claimed to have made compound **U**, which is an isomer of fumaric acid.



compound **U**



fumaric acid

State a reagent that would react with compound **U** and **not** fumaric acid, giving the result of the test. [1]

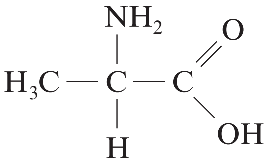
Total [20]

(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**.



$$H_3C-C(NH_2)(H)-C(=O)OH$$

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]

(iv) Draw the repeating unit in Nylon 6,6. [1]

(v) What type of condensation polymer is Nylon 6,6? [1]

....

(vi) A typical plant makes 800 tonnes of nylon per day. Given that the relative molecular mass of each repeating unit is 226 and assuming yields of 100% at each step, calculate the mass of benzene needed per day to produce this quantity of nylon. [2]

....

....

....

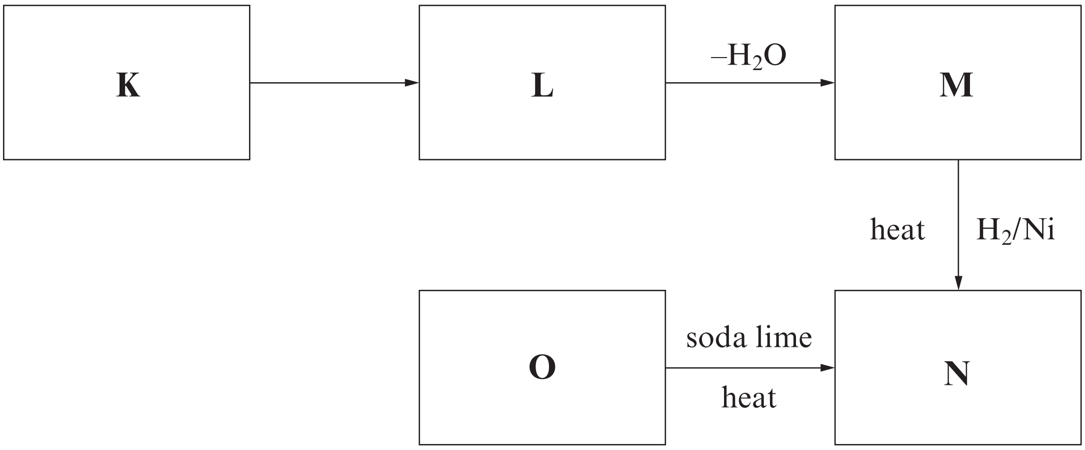
Total [15]

Total Section A [40]

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]

5. This question concerns isomers with molecular formula $C_5H_{10}O_2$.

(a) Isomers **P**, **Q**, **R** and **S** all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **P** is a straight-chain compound.

Isomer **Q** contains a chiral carbon centre.

Isomer **R** has only two peaks in its NMR spectrum, both of which are singlets.

Draw the displayed formulae for all **four** isomers. [4]

(b) Isomer **T** is a neutral, sweet-smelling compound and is formed by the reaction between compounds **X** and **Y** in the presence of concentrated sulfuric acid.

Compound **X** has an absorption in its infrared spectrum at 1750 cm^{-1} and a broad absorption around 3000 cm^{-1}.

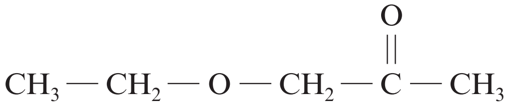
Compound **Y** can be formed directly from ethanal.

(i) Use **all** the information given to name compounds **X** and **Y**, giving your reasoning. Draw the displayed formula for isomer **T**. [4]
QWC [2]

(ii) I. State the reagent needed to form compound **Y** from ethanal. [1]

II. State the role of sulfuric acid in the formation of **T**. [1]

(c) Isomer **U** has the structural formula shown below.



$$CH_3-CH_2-O-CH_2-\overset{\overset{O}{||}}{C}-CH_3$$

List the peaks which would be found in the NMR spectrum of isomer **U**. Identify which protons are responsible for each peak, giving the approximate chemical shift (ppm) and the splitting of the peak. [4]

(d) Explain which one of isomers **P**, **T** and **U** would have the highest boiling temperature. [3]
QWC [1]

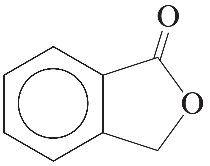
Total [20]

Section B Total [40]

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

Phthalides

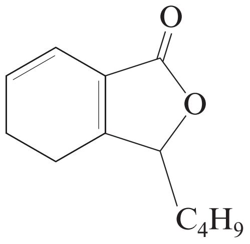
Phthalides are a family of compounds which are present in many plants, fungi and moulds. They are all based around the basic phthalide structure which has a benzene ring with a five-membered cyclic ester attached to it.



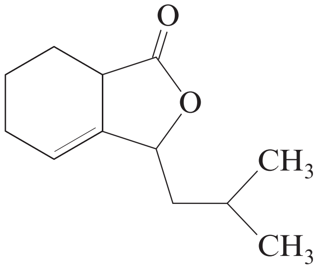
phthalide

Many phthalide-containing plants have been used worldwide as herbal remedies in traditional and folk medicines, and these have been found to affect many biological systems. 3-arylphthalides are also useful intermediates in the synthesis of anthracycline antibiotics.

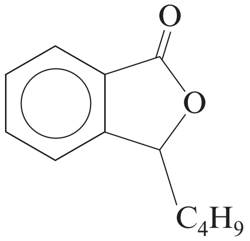
Some phthalides and their derivatives also act to enhance the flavour of food. In studies of celery, it was found that three particular compounds present in the plant had no flavour of their own, but enhanced the flavours of other foods when cooked together. These three were sedanenolide, sedanolide and 3-butylphthalide.



sedanenolide



sedanolide

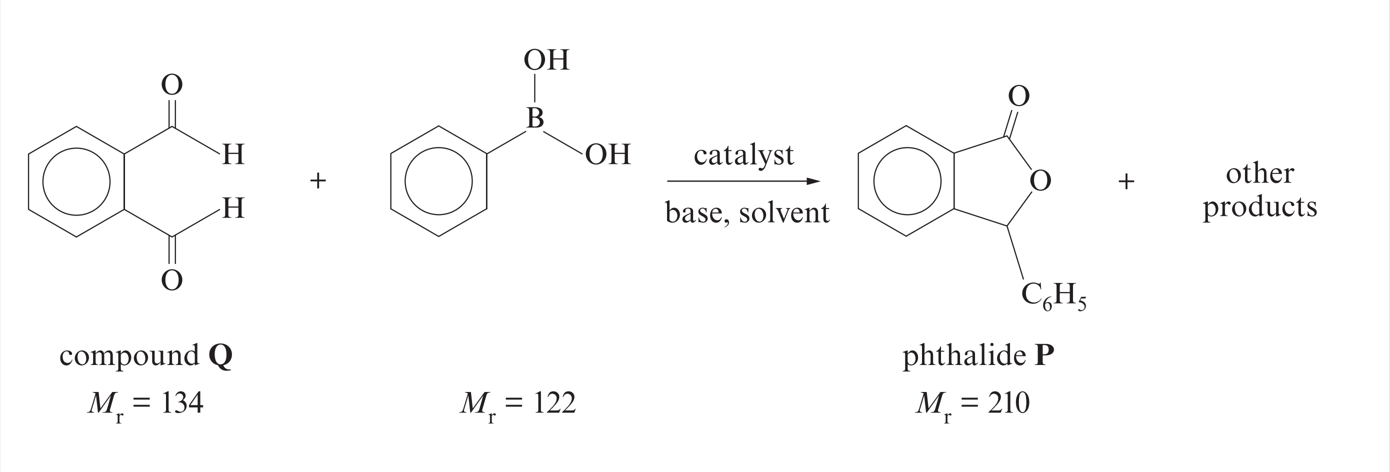


3-butylphthalide

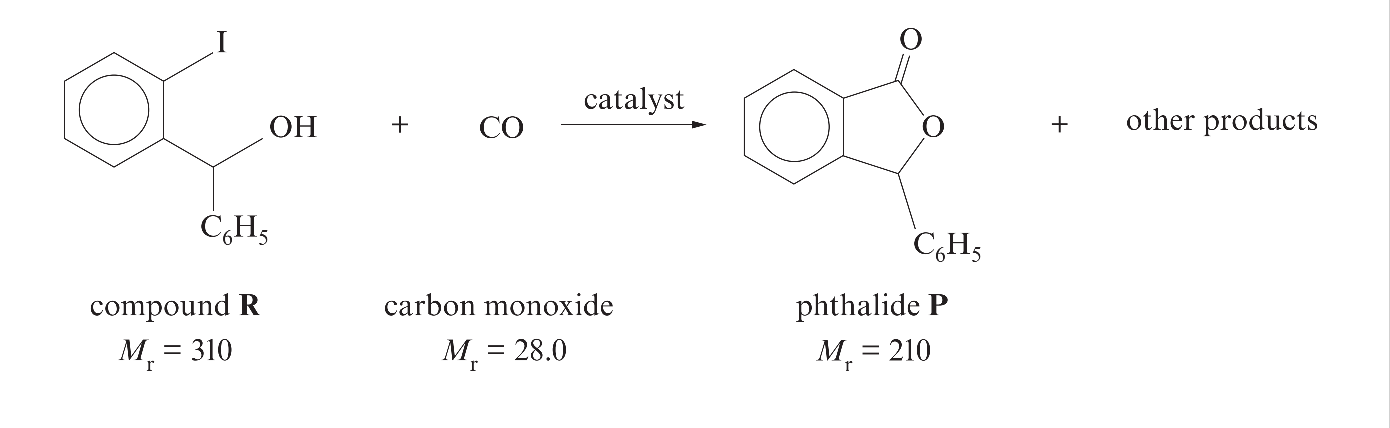
These molecules, amongst many others, are present in substantial amounts in oil of celery seed. These compounds are usually liquids with different boiling temperatures.

Due to the phthalide structure being a key part of useful molecules, there have been many attempts at synthetic routes to produce this structure. Two successful methods to form 3-phenylphthalide are shown as route 1 and route 2 opposite. Route 1 was developed more recently than route 2, and is considered to be a significant improvement. One reason for considering route 1 to be the better approach is the greater variety of different phthalides that can be produced by this method, whilst route 2 is only useful for a limited number of phthalides.

Route 1



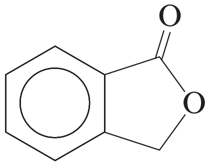
Route 2



– End of passage –

(a) Phthalides are considered to be cyclic esters *(line 3)*.

(i) Indicate the ester group on the diagram of phthalide below by drawing a circle around it. [1]

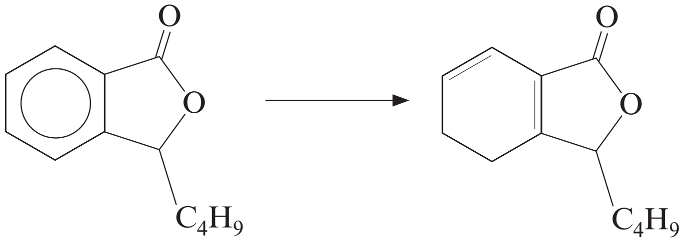


phthalide

(ii) Esters can be hydrolysed by heating with dilute sodium hydroxide solution. Draw the structure of the ion formed by hydrolysis of phthalide in this way. [1]

(b) Celery seed oil contains many different compounds *(lines 13-14)*. Suggest a method for obtaining pure samples of each different compound. [1]

(c) It is possible to convert 3-butylphthalide into sedanenolide in a hydrogenation reaction.



3-butylphthalide

sedanenolide

In this case the enthalpy change is +20 kJ mol^{-1}. The enthalpy change during hydrogenation of an alkene to form an alkane is typically –120 kJ mol^{-1}.
Explain this significant difference in enthalpy values for these two reactions. [2]

(d) The atom economy for route 1 to produce phthalide **P** is 82.0%.
Calculate the atom economy for route 2 to produce **P**. [1]

....

....

(e) Route 1 is considered to be the better of the two methods for producing phthalides *(line 18)*.

(i) Give **one** reason stated in the passage for considering route 1 to be the better method. [1]

....

....

(ii) Give **one** reason not stated in the passage for considering route 1 to be the better method. [1]

....

....

(f) Give a chemical test that would distinguish between compound **Q** and compound **R** *(page 9)*. Include any reagent(s) required and state the observations expected for **each** compound. [3]

Reagent(s) ....

Observations ....

....

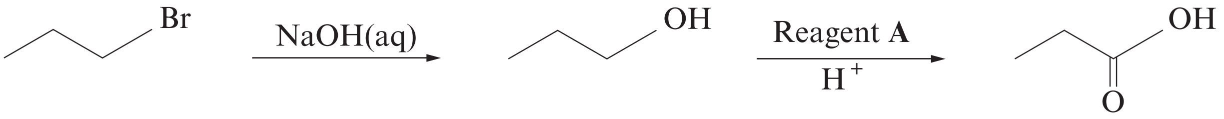
Total [11]

Total Section A [40]

SECTION B

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

4. *(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]

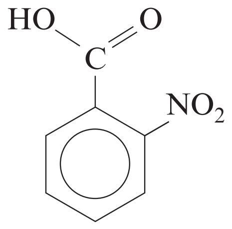
(ii) Compound **B** shows three resonances in its ^1_1H nuclear magnetic resonance spectrum.

- 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

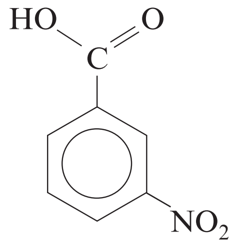
The infrared spectrum of compound **B** shows absorptions at 2981 cm^{-1} and 1750 cm^{-1}.
These are the only significant absorptions above 1500 cm^{-1}.
Using **all** the information supplied, deduce the structure of compound **B**.
Give **reasons** in support of your answer. [5]
(QWC) [2]

Total [20]

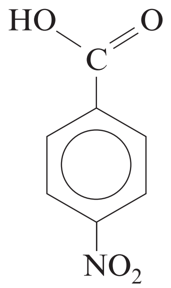
5. *(a)* Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



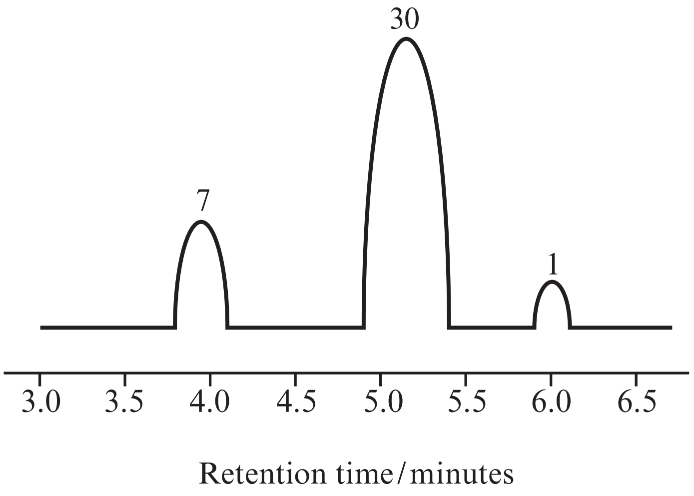
3-nitrobenzoic acid



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.



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]

(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]

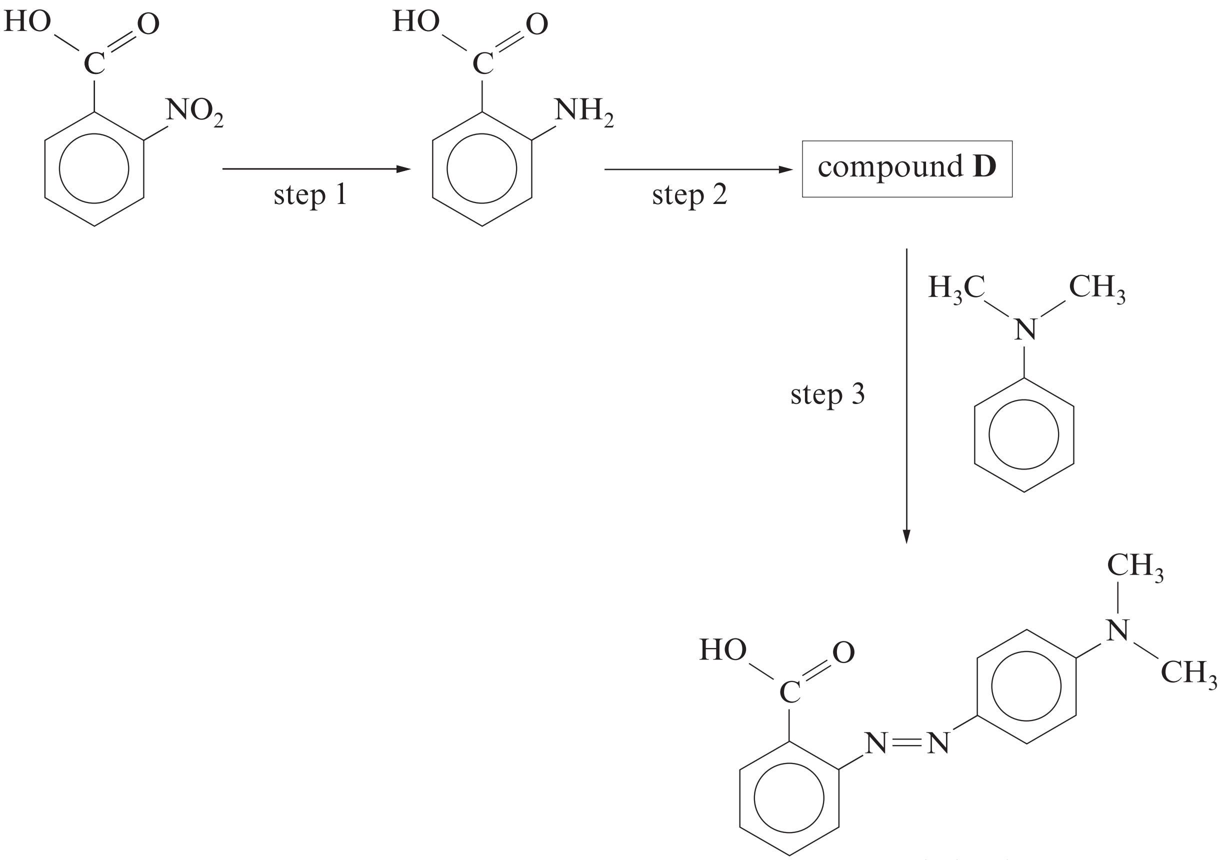
II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

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

(QWC) [1]

QUESTION 5 CONTINUES ON PAGE 16

(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.



(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]

SECTION B

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

4. *(a)* Today there are thousands of different polymers and they are used in a wide range of applications.

Describe the formation of **one** synthetic polymer and **one** natural polymer, both made by condensation polymerisation.

Your answer should include

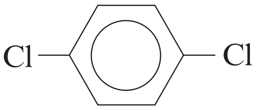
- the names or structures of the starting materials required for both polymers,
- a structure which shows the repeating unit for the synthetic polymer,
- a structure which shows the relevant linkage in the natural polymer. [5]

QWC [1]

(b) **F** and **G** are two organohalogen compounds.

(chloromethyl) benzene

F



G

Compound **F** is used in the manufacture of plasticizers and perfumes and behaves as a chloroalkane. Compound **G** is used as a pesticide and as a deodorant.

(i) Draw the displayed formula of compound **F**. [1]

(ii) Name compound **G**. [1]

(iii) State the reagent(s) and condition(s) needed to substitute a chlorine atom into a benzene ring. [2]

(iv) Describe how you could use a chemical test to distinguish between compounds **F** and **G**. Give the expected result for **each** compound and an explanation for any difference in their behaviour. [6]

QWC [1]

(c) Benzenediazonium chloride can be prepared as follows.
Phenylamine is dissolved in excess hydrochloric acid and the solution cooled to 5 °C.
Aqueous sodium nitrate(III), $NaNO_2$, is added gradually until in excess, keeping the temperature at approximately 5 °C.

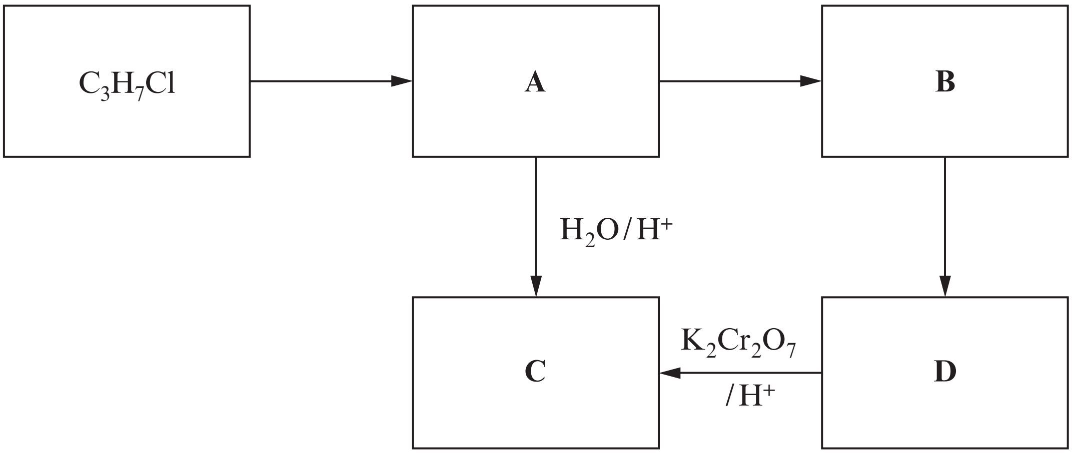
(i) State why the temperature is kept under 10 °C. [1]

(ii) Give the displayed formula of the compound that forms when benzenediazonium chloride reacts with naphthalene-2-ol in alkaline conditions. [1]

(iii) State what is meant by the term *chromophore*. [1]

Total [20]

5. *(a)* Study the reaction scheme shown below and the other information about compounds **A**-**D** that follows.



Compound **A** contains a straight carbon chain and contains only carbon, hydrogen and nitrogen.

Compound **B** is basic and reacts with hydrochloric acid in a 1:1 molar ratio.

0.395 g of compound **B** in aqueous solution requires 54.00 cm^3 of hydrochloric acid solution of concentration 0.100 mol dm^{-3} for complete neutralisation.

Compound **C** reacts with sodium carbonate giving off carbon dioxide.

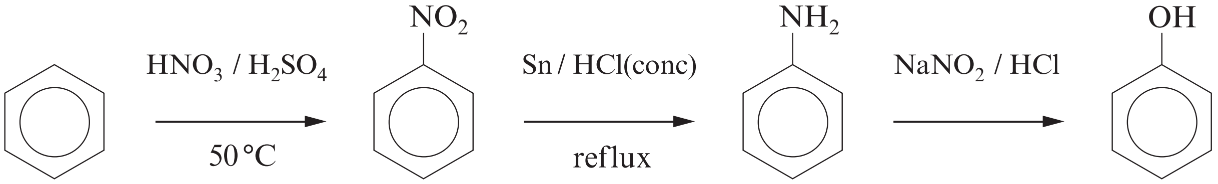
(i) Calculate the relative molecular mass of compound **B**. Show your working. [2]

(ii) Identify the structures of compounds **A**-**D**, giving your full reasoning. [8]

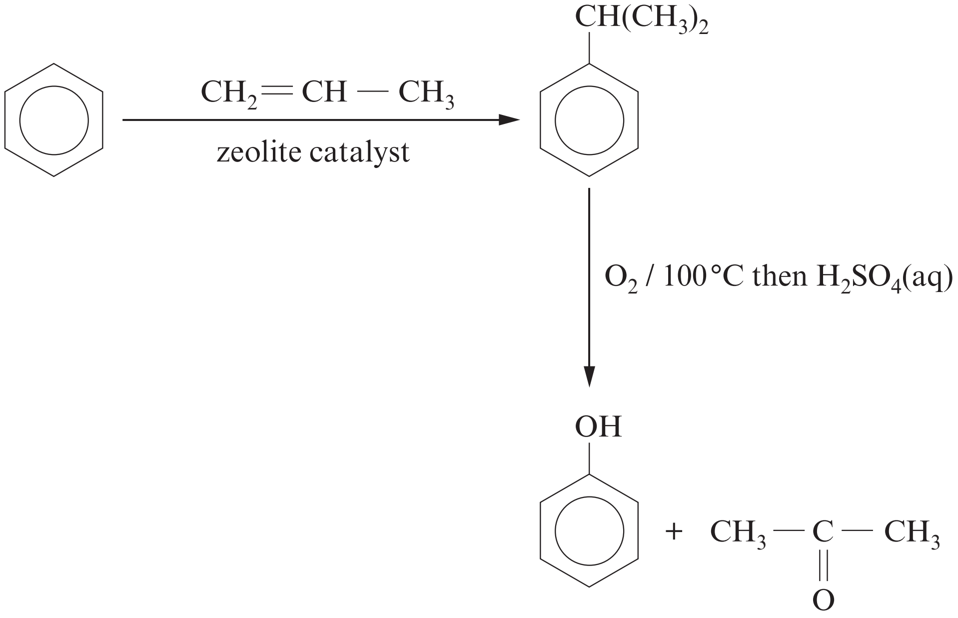
(b) C_3H_7Cl exists as two isomers. Sketch the **low** resolution NMR spectra of both isomers giving the approximate chemical shift (ppm) and the relative area of each peak. [4]

QUESTION 5 CONTINUES ON PAGES 14 AND 15

(c) Phenol can be made by the following three-step synthesis.



However, the industrial method of making phenol uses a different route as shown below.



(i) Give **two** possible advantages of the industrial route. [2]

(ii) Until 1995 solid phosphoric acid was used as the catalyst for the first stage of the industrial route. Suggest a reason, apart from an increased reaction rate, why this was changed to a zeolite catalyst. [1]

(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]

13

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]

....

....

....

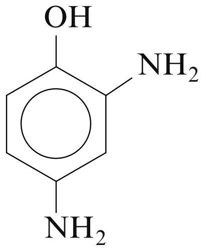
(b) 2,4-Dinitrophenol is a yellow solid that is an inhibitor of ATP production in cells. As a result it has been sold as an aid to slimming, in spite of it being a dangerous and unlicensed product.

(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'.

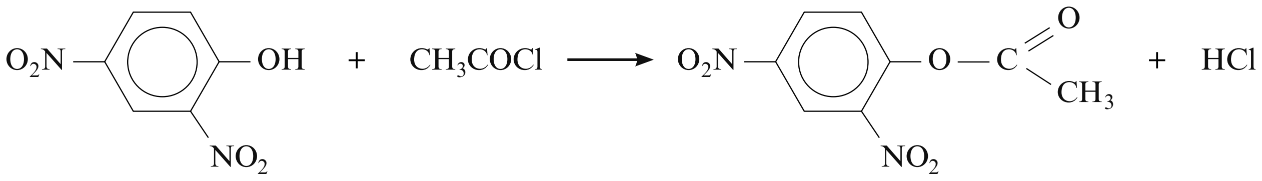


amidol

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

....

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

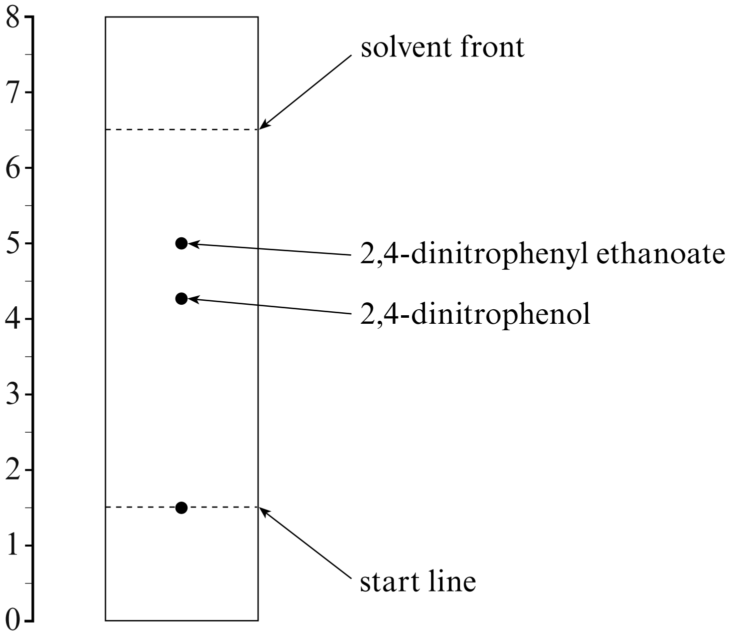


$M_r = 184$ $M_r = 226$

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.



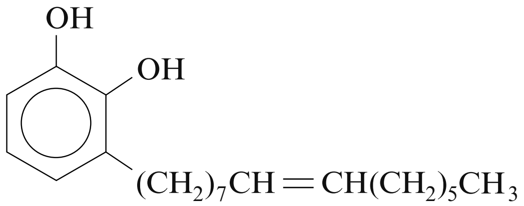
Calculate the R_f value of 2,4-dinitrophenol from this chromatogram. [2]

....

....

....

(d) 'Urushiol' is a yellow liquid that is found in the plant poison ivy. It causes an allergic skin rash. Urushiol is not a single compound but a mixture of phenolic compounds that have long saturated or unsaturated alkyl groups bonded to the benzene ring.
It contains, for example, the following compound.



(i) Suggest a catalyst that could be used in the hydrogenation of the unsaturated alkyl side chain. [1]

....

(ii) By analogy with carboxylic acids, explain why 1,2-dihydroxybenzene is soluble in water but urushiol is not. [2]

....

....

....

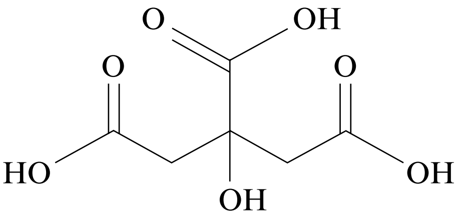
Total [12]

12

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.



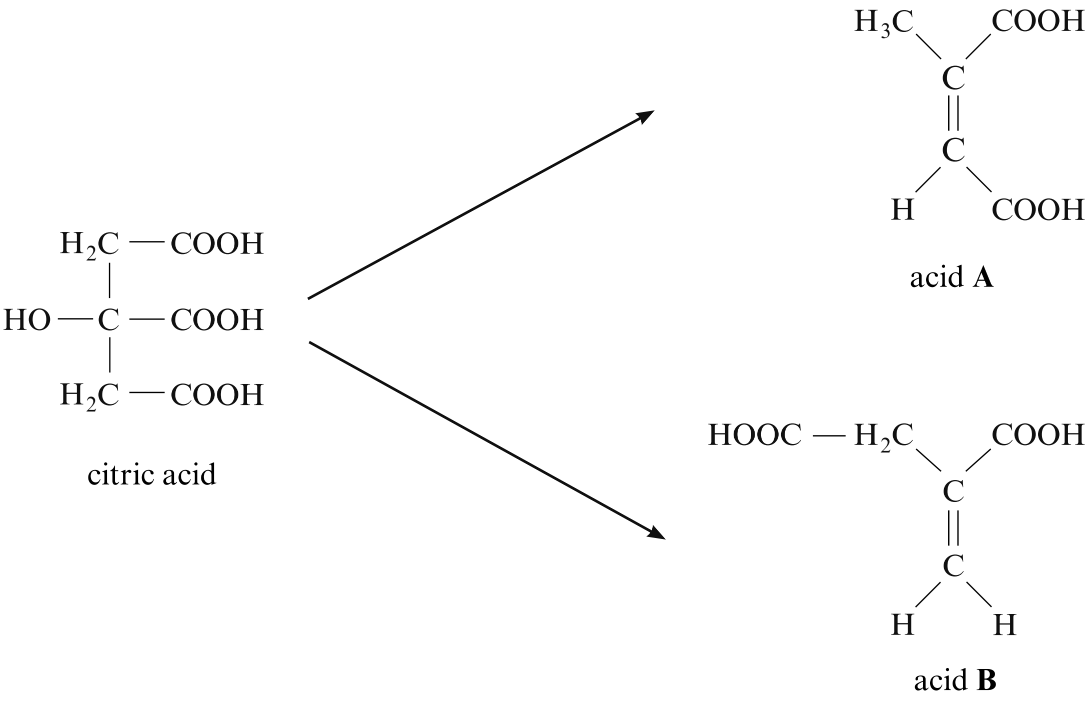
$M_r = 192$

citric acid

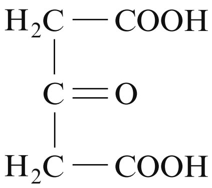
This acid has been known since the 8th century and from about 1890 it began to be isolated from citrus fruits. The concentration of citric acid in the juices of these fruits varies from about 0.005 mol dm^{-3} for oranges to 0.300 mol dm^{-3} for lemons. However, most citric acid is now made from sugars 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.

$$\underset{\substack{\text{calcium citrate} \\ M_r = 498}}{(C_6H_5O_7)_2Ca_3} + \underset{M_r = 98}{3H_2SO_4} \longrightarrow \underset{M_r = 192}{2C_6H_8O_7} + 3CaSO_4$$

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

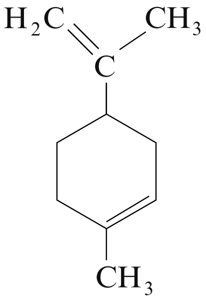


When citric acid is treated with concentrated sulfuric acid, acid **C** is formed.

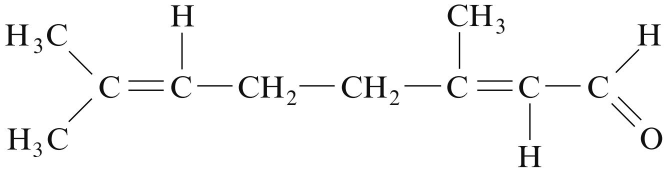


acid **C**

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 –

(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]

....

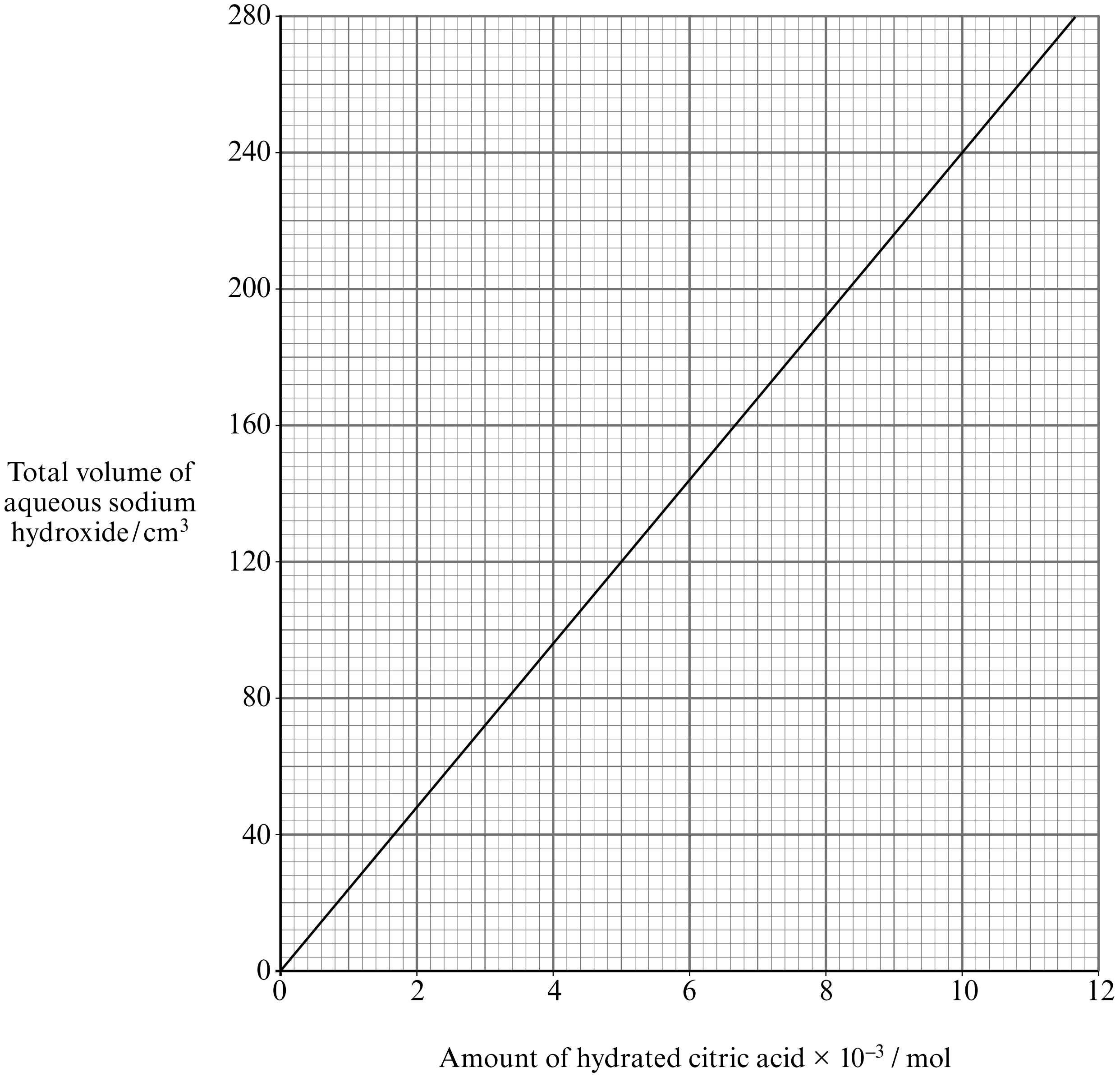
....

(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 =..



(c) Explain why acids **A** and **B** *(line 13)* are **not** *E*- and *Z*- isomers of each other. [1]

....

....

(d) Acids **A** and **B** are formed by dehydration and by decarboxylation (where the compound is heated with sodalime). Give any other decarboxylation reaction of your choice, stating the organic starting material and the organic product of your chosen reaction. [2]

(e) On heating to 130 °C, acid **C** *(line 15)* decomposes to give only propanone and carbon dioxide. Give the equation for this reaction. [1]

(f) Give the **displayed** formula of the product formed when acid **C** is reduced by lithium tetrahydridoaluminate(III) (lithium aluminium hydride). [1]

(g) The boiling temperatures of limonene and citral, both present in lemon oil, are 177 °C and 228 °C respectively. State a method by which these two liquids can be separated. [1]

(h) Limonene occurs in some substances as a single enantiomer and in others as a racemic mixture.

(i) State what is meant by the term *enantiomer*. [1]

(ii) State what is meant by the term *racemic mixture*. [1]

Total [15]

Total Section A [40]

15

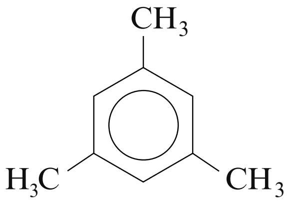
SECTION B

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

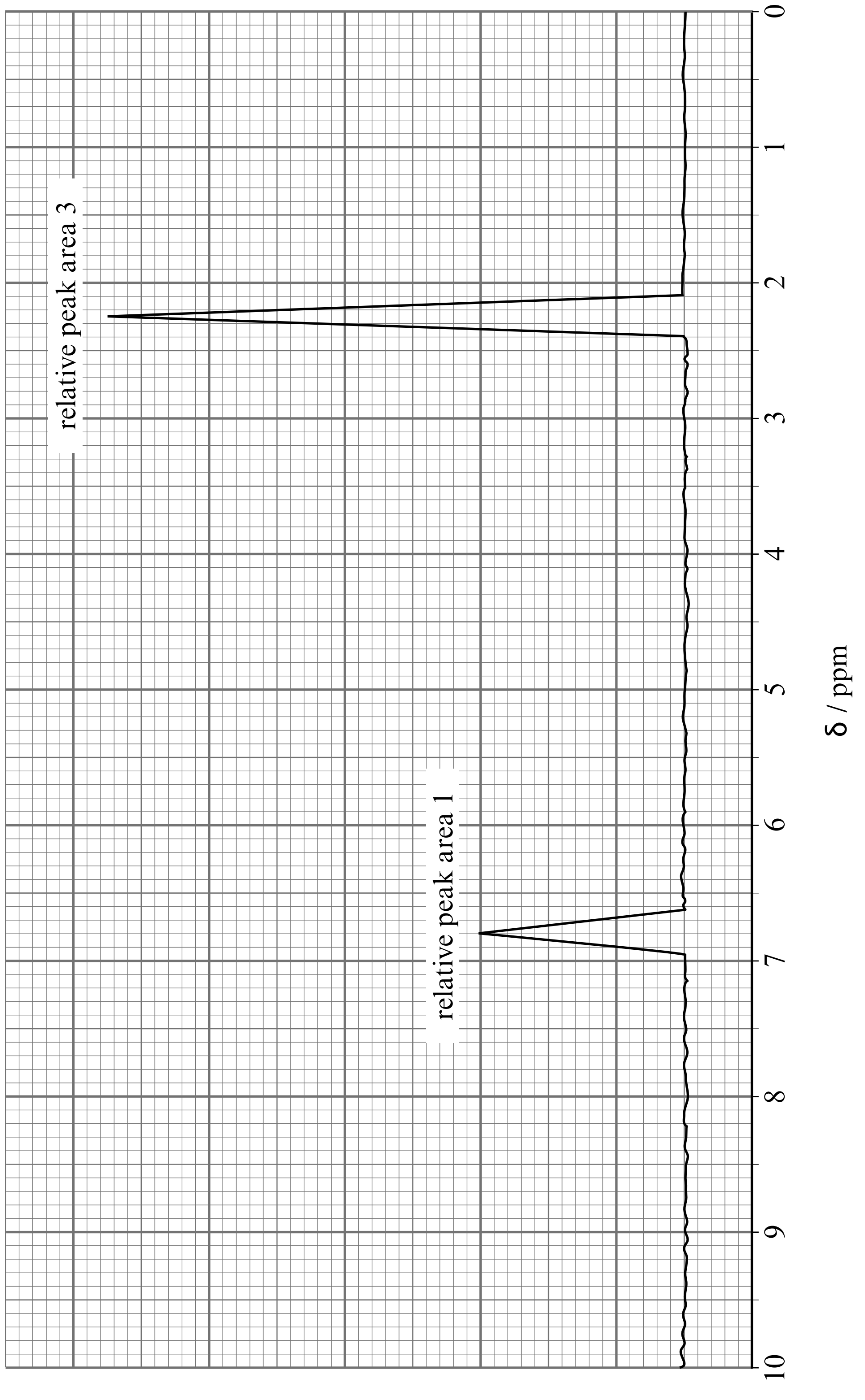
4. *(a)* Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions. [6]
QWC [2]

(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]

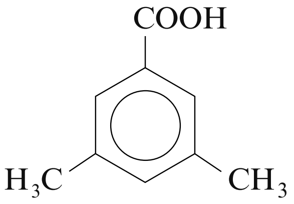
(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.



(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]


relative peak area 3
relative peak area 1
0
1
2
3
4
5
6
7
8
9
10
δ / ppm

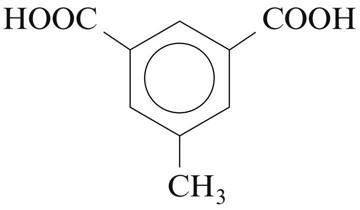
(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



melting temperature 172 °C

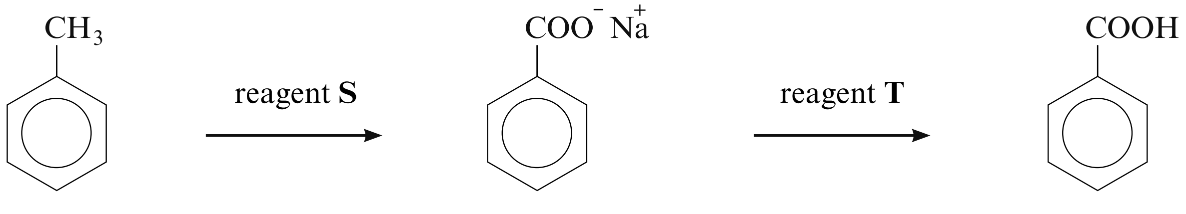
Describe how you would purify a sample of this acid by recrystallisation.
The acid is fairly soluble in hot water but nearly insoluble in cold water. [4]

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



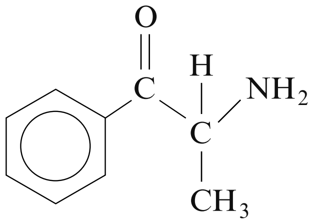
By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol. [1]

(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]

5. *(a)* Cathinone, $C_9H_{11}NO$, is a naturally-occurring psycho-active drug.



(i) Explain why this molecule can act as a base. [1]

(ii) You are provided with some information about an **isomer** of cathinone, compound **L**.

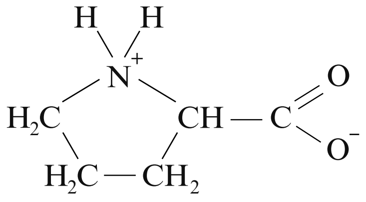
- It contains a peptide linkage.
- It can be hydrolysed by aqueous sodium hydroxide giving primary aromatic amine **M** as one of the products.
- Primary aromatic amine **M** reacts with nitric(III) acid (nitrous acid) to give a phenol with the molecular formula C_7H_8O.

Use **all** this information to suggest a **structural** formula for compound **L**, giving your reasons throughout. [6]

QWC [1]

QUESTION 5 CONTINUES ON PAGES 18 AND 19

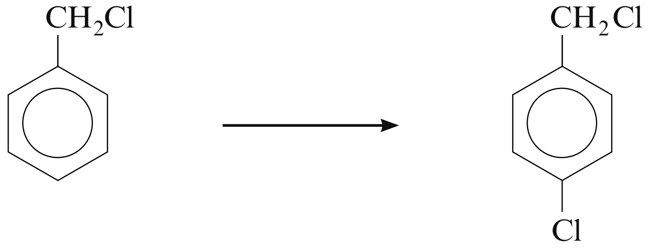
(b) Proline is a cyclic α-amino acid. In an aqueous solution of pH 6.3, proline exists largely as its zwitterion form.



(i) Write the structural formula of proline in its non-zwitterion form. [1]

(ii) Proline forms two different dipeptides when it reacts with aminoethanoic acid. Give the structural formula of **one** of these dipeptides. [1]

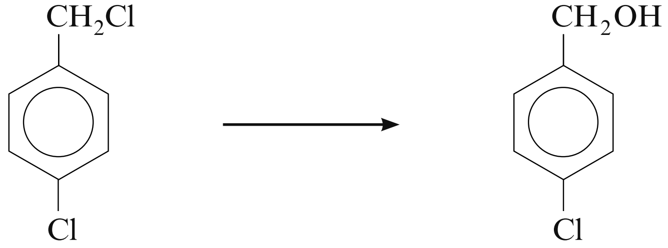
(c) (i) (Chloromethyl)benzene, $C_6H_5CH_2Cl$, reacts with chlorine in the presence of a catalyst to produce a mixture of isomers, **one** of which is 1-(chloromethyl)-4-chlorobenzene.



The mechanism of this electrophilic substitution reaction is similar to the reaction of benzene with chlorine. Give the mechanism for the reaction to produce the 4-isomer.

Your mechanism should show any necessary polarisation, curly arrows, the structure of the intermediate and how the catalyst is regenerated so that it can be used again. [4]

(ii) A student made (4-chlorophenyl)methanol by refluxing 1-(chloromethyl)-4-chlorobenzene (shown in (i)) with aqueous sodium hydroxide.
He obtained a 72% yield.

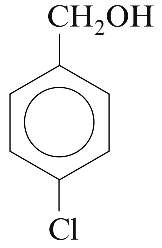


He wrote an outline of his method as follows.

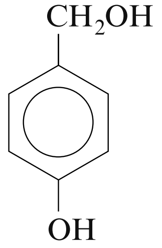
- Place 0.1 mol of the chloro-compound in a flask and add some sodium hydroxide solution of concentration 2 mol dm^{-3}.
- Reflux this mixture using an electrical heater.

Suggest **two** other details that you would need to know before you could test the reliability and validity of his method. [2]

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

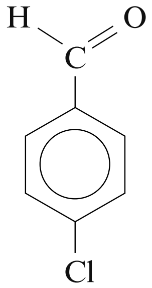


(4-chlorophenyl)methanol



(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

2. 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]

....

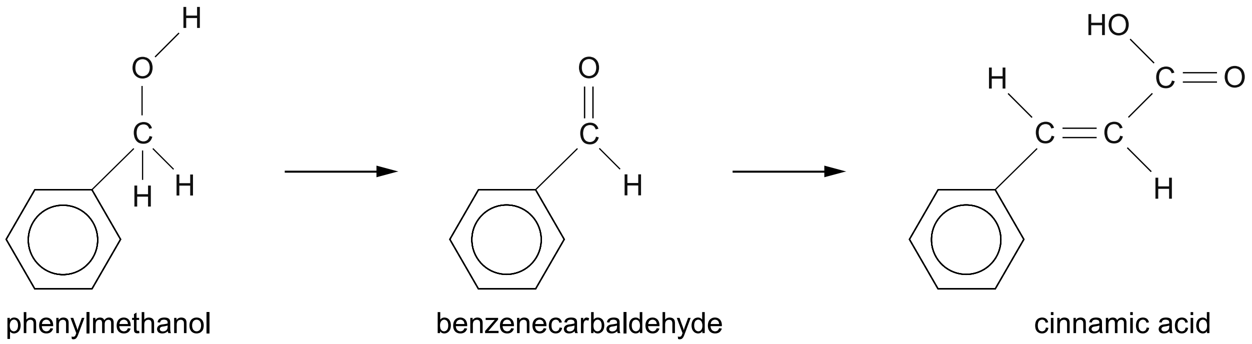
....

....

....

Examiner only

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



(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]

....

....

....

....

....

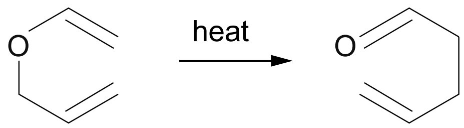
Total [13]

13

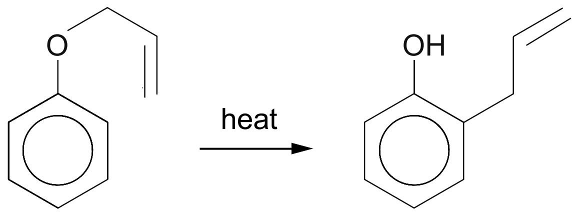
3. *Read the passage below and then answer the questions in the spaces provided.*

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.



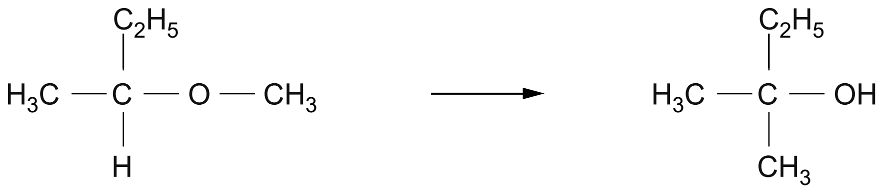
Claisen rearrangement



aromatic Claisen rearrangement

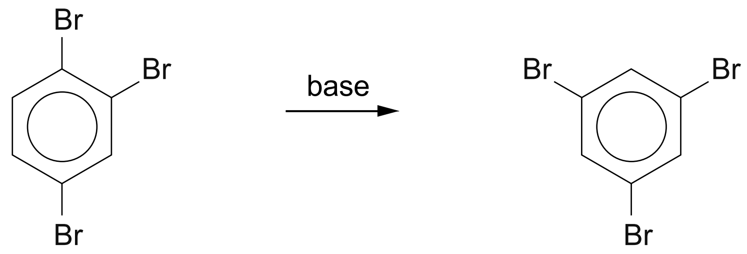
This rearrangement can occur in a wide range of molecules, and so it is used in the production of a number of biologically active molecules including *Pancratistatin* and *Halomon*, both of which have antitumour activity. The rates of these reactions are much higher in polar solvents, especially those 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.



$$H_3C-\overset{C_2H_5}{\underset{H}{C}}-O-CH_3 \longrightarrow H_3C-\overset{C_2H_5}{\underset{CH_3}{C}}-OH$$

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 –

(a) The products of rearrangement reactions have the same molecular formulae as the reactants *(lines 3-4)*. State the term given to different molecules that share the same molecular formula. [1]

(b) A chemist used infrared spectroscopy to study the factors that affect the rate of the aromatic Claisen rearrangement shown in *line 7*.

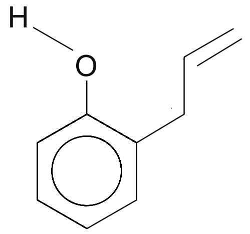
(i) Give the difference(s) between the infrared spectra of the reactant and product. [1]

(ii) Give the reagent(s) and observation(s) for a chemical test that would show that the product is a phenol. [2]

Reagent(s)

Observation(s)

(iii) The reaction is faster in solvents that can form hydrogen bonds, such as methanol or water *(lines 10-11)*. Draw the hydrogen bonding that can occur between the product shown and a molecule of water. [2]



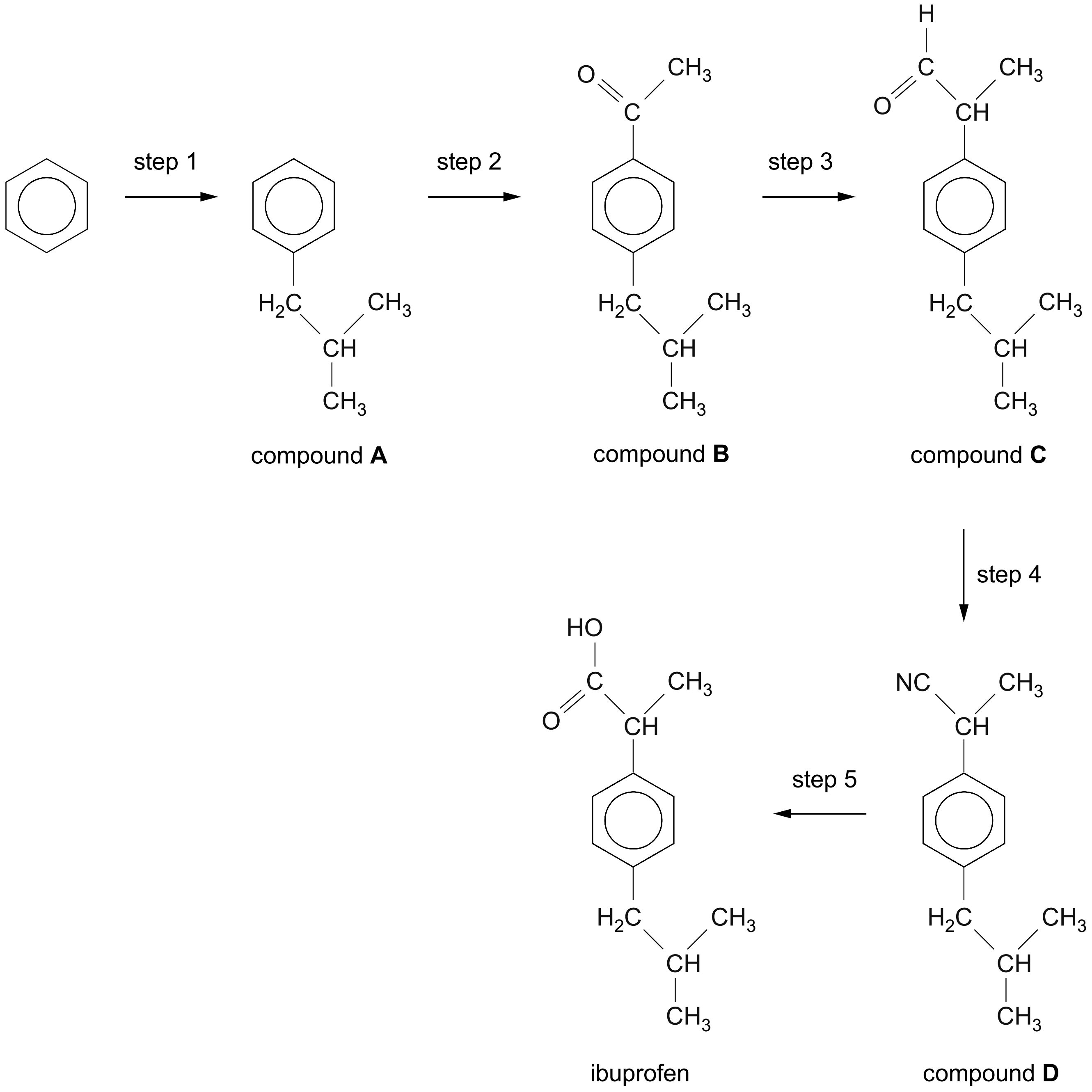
(c) The products of the aromatic Claisen and 1,2-Wittig rearrangements shown *(lines 7* and *17)* both contain —OH groups. Explain why the acidity of the two molecules is very different. [3]
QWC [1]

SECTION B

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

4. Ibuprofen is a common drug taken as an analgesic and anti-inflammatory treatment.

A possible route to the synthesis of ibuprofen is shown below.



(a) Step 1 is a Friedel-Crafts alkylation reaction. Give the reagent(s) and condition(s) required for this step. [3]

(b) Compounds **B** and **C** can be analysed using chemical tests.

(i) Give a chemical test that would give a positive result for **both** compound **B** and compound **C**. Include reagent(s) and the observation(s) expected for a positive result. [2]

(ii) Give a chemical test that would give a positive result for compound **C** but **not** for compound **B**. Include reagent(s) and the observation(s) for both compounds. [2]

(c) Compound **C** shows optical isomerism. Discuss this statement.
Your answer should include:

- What is meant by optical isomerism.
- What feature of compound **C** allows it to exhibit optical isomerism.
- Diagrams to show the two optical isomers of compound **C**.
- How the two optical isomers of compound **C** can be distinguished. [4]

QWC [1]

(d) Give the reagent(s) and condition(s) required for step 5 and classify the reaction that occurs. [3]

(e) A student investigating alternative methods of producing ibuprofen suggests that it would be better to convert compound **C** into ibuprofen in a one-step process. Discuss whether this is correct.
Your answer should include:

- The reagent(s) and condition(s) for a reaction expected to convert compound **C** directly into ibuprofen.
- Why it is generally better to use one step rather than two or more steps when producing a desired compound.
- A suggestion of why a two-step process is chosen for the synthesis of ibuprofen from compound **C** rather than a one-step process. [4]

QWC [1]

Total [20]

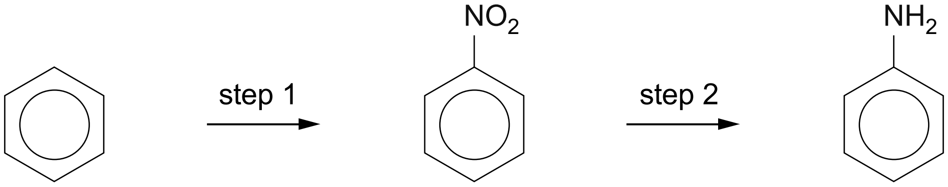
5. This question focuses on molecules that contain the —NH_2 group.

(a) Phenylamine and propylamine are both bases, with phenylamine being a weaker base than propylamine.

(i) Explain why both propylamine and phenylamine can act as bases. [2]

(ii) Give a reason why phenylamine is a weaker base than propylamine. [2]

(iii) Phenylamine can be prepared from benzene in a two-step process.



I. Step 1 uses a mixture of concentrated nitric and sulfuric acids to produce NO_2^+ during the reaction. Draw the mechanism of the reaction between NO_2^+ and benzene. [3]

II. During step 1, some dinitrobenzene is produced. Suggest a method of separating the different compounds in the product mixture. [1]

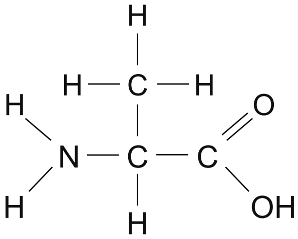
III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]

(b) 1,6-diaminohexane is used to make Nylon-6,6, which is a polyamide.

(i) Draw the **skeletal** formula for the molecule that would be combined with 1,6-diaminohexane to make Nylon-6,6. [1]

(ii) Nylon is an example of a condensation polymer. Give **two** differences between condensation polymerisation and addition polymerisation. [2]

(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]

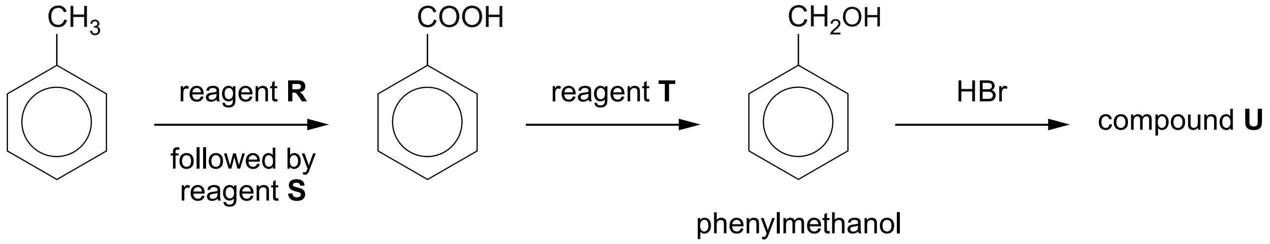
Total [20]

Total Section B [40]

END OF PAPER

(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]

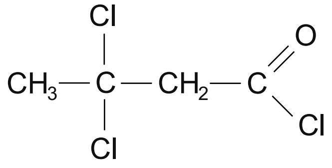
(iii) State the name of reagent **T**. [1]

(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]

(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 pattern [3]

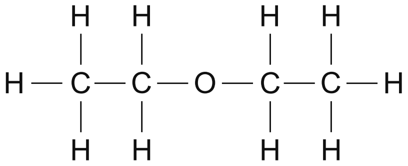
QWC [1]

Total [13]

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

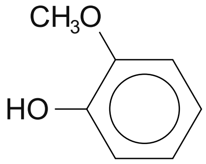
The chemistry of some compounds containing the ether (R–O–R) linkage

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.

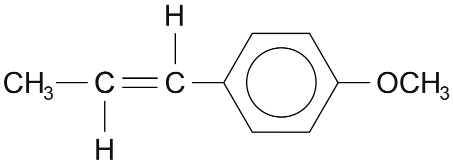


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

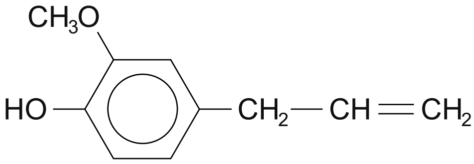
ethoxyethane



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.

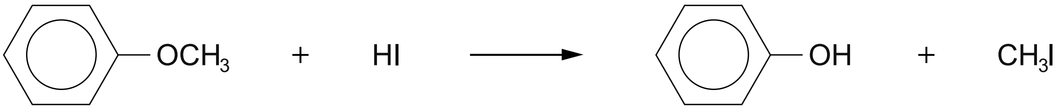
$$2CH_3CH_2OH \xrightarrow{-H_2O} CH_3CH_2OCH_2CH_3$$

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

$$CH_3CH_2Br \quad + \quad \underset{\text{ethoxide ion}}{{}^{-}OCH_2CH_3} \longrightarrow CH_3CH_2OCH_2CH_3 \quad + \quad Br^{-}$$

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

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 -

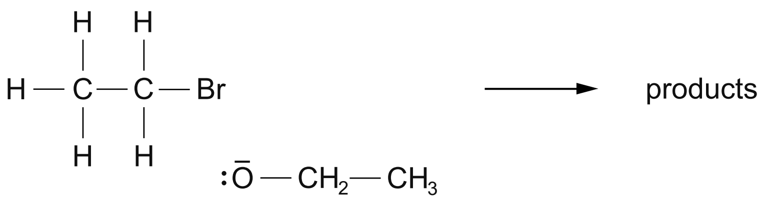
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol ($M_r = 46$) and obtained a 45 % yield of ethoxyethane ($M_r = 74$). Calculate the mass of ethoxyethane obtained. [3]

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]

....

....

(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]

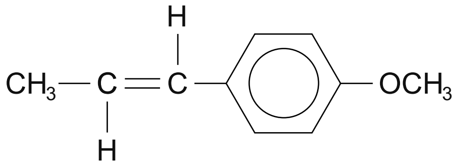
Reagent ....

Observation ....

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

....

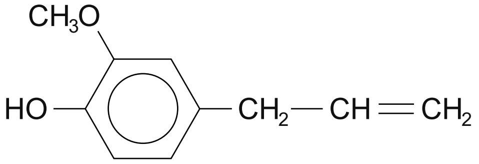
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



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]

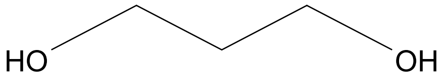
Total Section A [40]

5. *(a)* An Australian cockroach protects itself from attack by spraying predators with an unpleasant unsaturated compound **E**. Analysis of this unsaturated compound, which is not cyclic, gave the following information.

- It contains C, 71.3 % and H, 9.6 % by mass. The remainder is oxygen.
- Only one oxygen atom is present in each molecule.
- It gives a silver mirror with Tollens' reagent (ammoniacal silver nitrate solution).
- The mass spectrum shows a fragmentation ion, containing only carbon and hydrogen, at m/z 29.

Use **each** piece of information to help you deduce a possible displayed formula for compound **E**. [6]

(b) Propane-1,3-diol is a starting compound for the manufacture of some economically important materials.



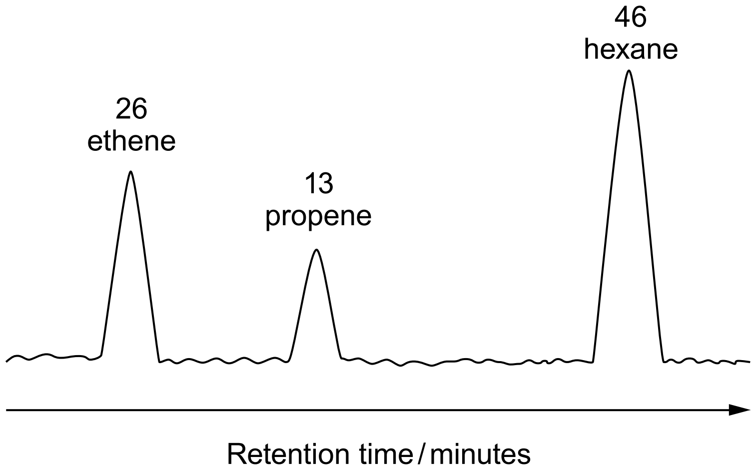
One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.

propene $\xrightarrow{O_2 \text{ (from air)}}$ propenal $\xrightarrow{\text{hydration}}$ propane-1,3-diol

A newer method uses a strain of the bacterium *E. coli* to obtain propane-1,3-diol directly from maize.

(i) Give the equation for the cracking of undecane, $C_{11}H_{24}$, into hexane, ethene and propene. [1]

(ii) A simplified gas chromatogram for the cracking of undecane is shown below.



The peak areas indicate the relative volumes of each compound.
Use the chromatogram to calculate the percentage by volume of propene present. [1]

(iii) You are a research chemist investigating the production of propane-1,3-diol from a cereal. Suggest **three** features of the process that could encourage your company to adopt this biochemical process, rather than the older process starting with propene. A simple reference to reduced costs is insufficient. [3]

(iv) Compound **W** is formed when propane-1,3-diol is heated with ethanoic acid in the presence of a suitable catalyst. It has the molecular formula $C_7H_{12}O_4$.
Give the displayed formula of compound **W**. [1]

(c) The polyester PET is made from ethane-1,2-diol and benzene-1,4-dioic acid. In a similar way PTT is made from propane-1,3-diol and benzene-1,4-dioic acid.

(i) Give the formula of the repeating unit of PTT. [1]

(ii) State how this type of polymerisation differs from the type of polymerisation occurring when poly(propene) is made from propene.
In your answer you should

- state the type of polymerisation occurring in each case,
- state the type of functional groups present in the starting materials for each process,
- compare the atom economy of each process. [6]

QWC [1]

Total [20]

Total Section B [40]

END OF PAPER