WJEC EDUQAS A-LEVEL CHEMISTRY · COMPONENT 2

CHEMISTRY



EXAM QUESTION PACK

OA4 ORGANIC SYNTHESIS AND ANALYSIS

SCORE	PERCENTAGE
/168	%

STEMUP

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

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

[1]

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

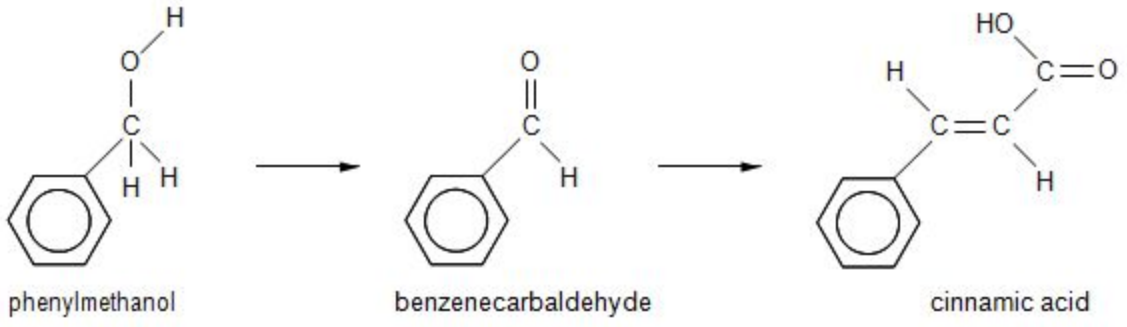
(i) Iwan used the melting temperature of the sample to confirm that the sample was impure. Give **one** way that the melting temperature would show this.

[1]

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

[2]

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



phenylmethanol benzenecarbaldehyde cinnamic acid

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

[2]

Reagent(s) . . . . . .

Condition(s) . . . . . .

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

[3]

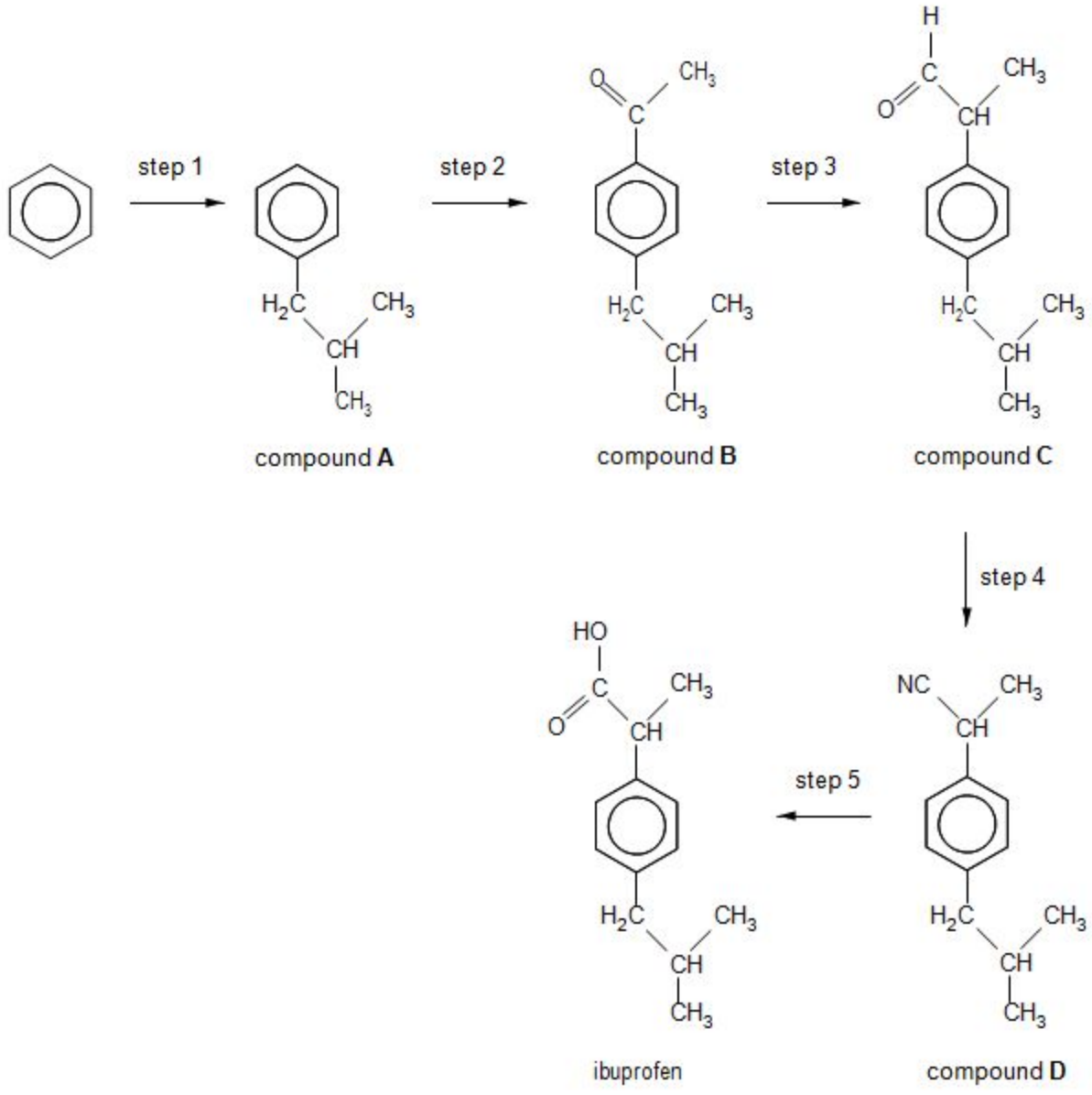
Mass=. . . . . g

(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]

2. 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.

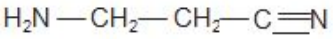
Your answer should include:

- 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.

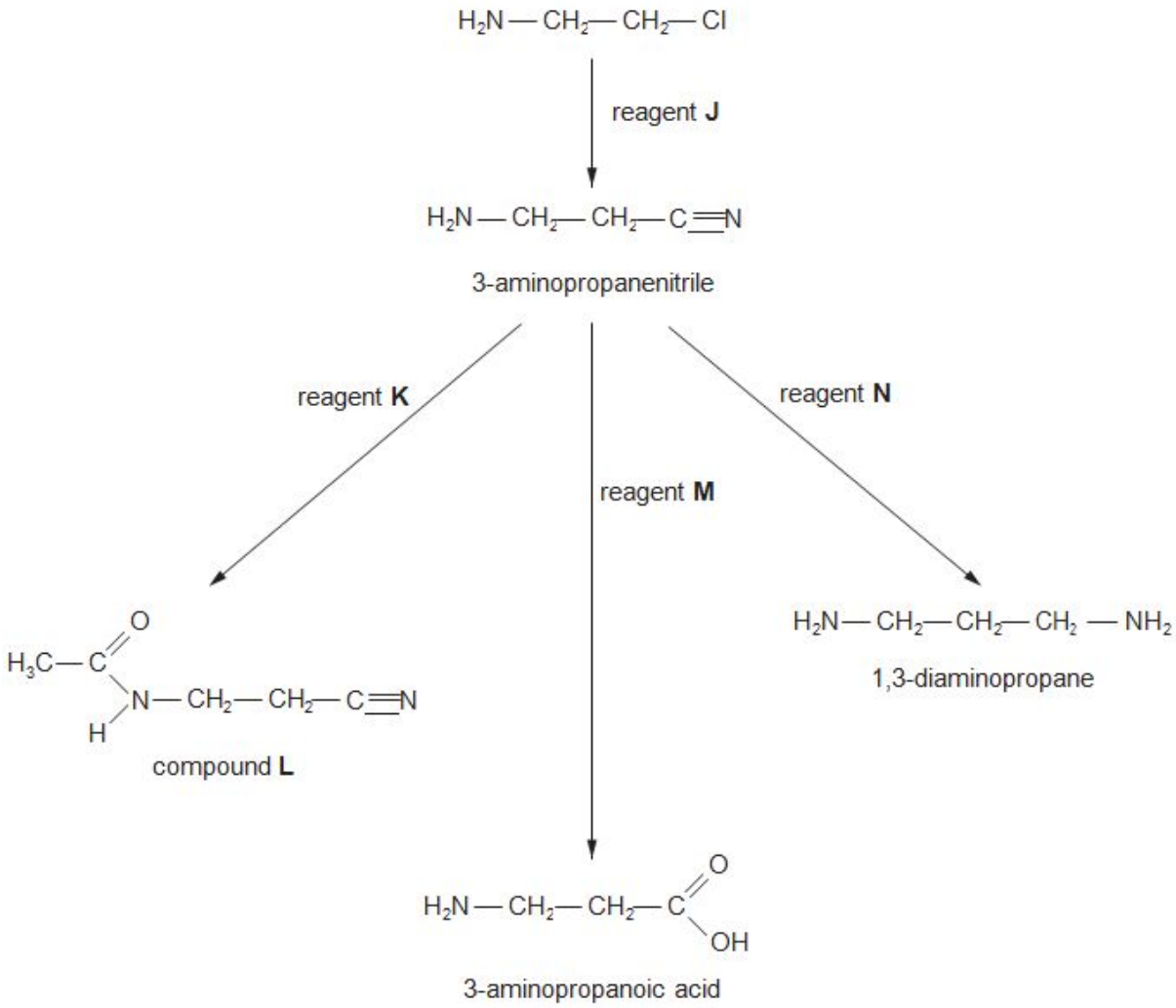
[4] QWC [1]

(Total 20)

3. *(a)* Seeds of the sweet pea plant contain 3-aminopropanenitrile.



One method of preparation of this compound and some of its reactions are outlined below.



(i) State the name of reagent **J.**

[1]

(ii) Give the displayed formula of reagent **K** that is used to produce compound **L** from 3-aminopropanenitrile.

[1]

(iii) State the name of reagent **M**, which is used in aqueous solution.

[1]

(iv) Although 3-aminopropanoic acid is not an α-amino acid, it exists as a zwitterion in a similar way to an a-amino acid.

Give the displayed formula of the zwitterion form of 3-aminopropanoic acid.

[1]

(v) 3-Aminopropanoic acid and compound **X** are isomers of formula $C_3H_7NO_2$. However, only compound **X** produces a silver mirror when reacted with Tollens' reagent. Suggest a displayed formula for compound **X**. [1]

(vi) State the formula of reagent **N.**

[1]

(vii) State why amines such as 1,3-diaminopropane are able to act as bases.

[1]

(b) Care has to be taken when collecting fungi for consumption as many of them contain poisonous compounds. An Asian mushroom contains a very toxic compound **G**. Some information about compound **G** is given below.

- It is an alicyclic compound (a **ring** compound of carbon atoms that is not aromatic)
- Its empirical formula is C_2H_2O
- It is an unsaturated compound
- It contains one carboxylic acid group, whose carbon atom is not part of the ring structure
- All the oxygen atoms present are in the carboxylic acid group
- The proton NMR spectrum shows 3 peaks whose relative peak areas are 1:1:2

Answer the questions below, which lead you through the information to help you find the displayed formula for compound **G**.

(i) Give the molecular formula for compound **G**...

[1]

(ii) Since one of the carbon atoms present is not part of the ring structure, the number of carbon atoms in the ring is...

[1]

(iii) Compound **G** is an unsaturated compound and therefore the ring must contain the functional group...

[1]

(iv) The peak areas in the NMR spectrum are 1:1:2. The carboxylic acid group proton is responsible for a peak area 1.

The remaining peak area ratio 1:2 suggests that…

[1]

(v) Use the information from parts (i) to (iv) to suggest the displayed formula for compound **G**.

[1]

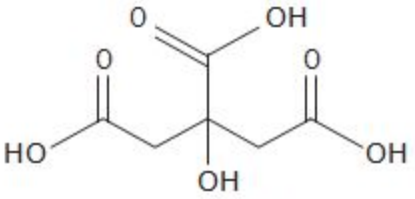
(Total 12)

4.

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.



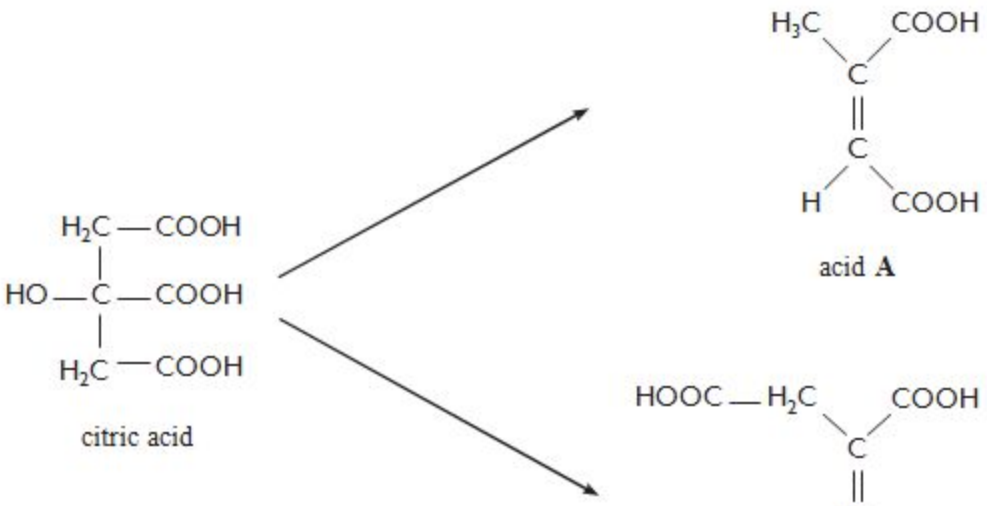
$M_r = 192$

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.



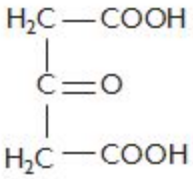
citric acid

acid **A**

acid **B**

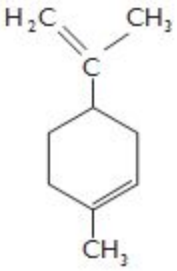
When citric acid is treated with concentrated sulfuric acid, acid **C** is formed.

15

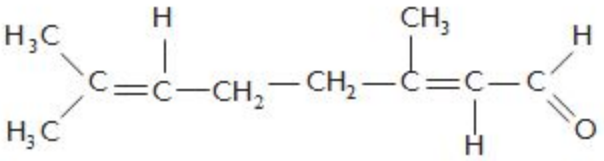


acid **C**

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

20 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]

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

[1]

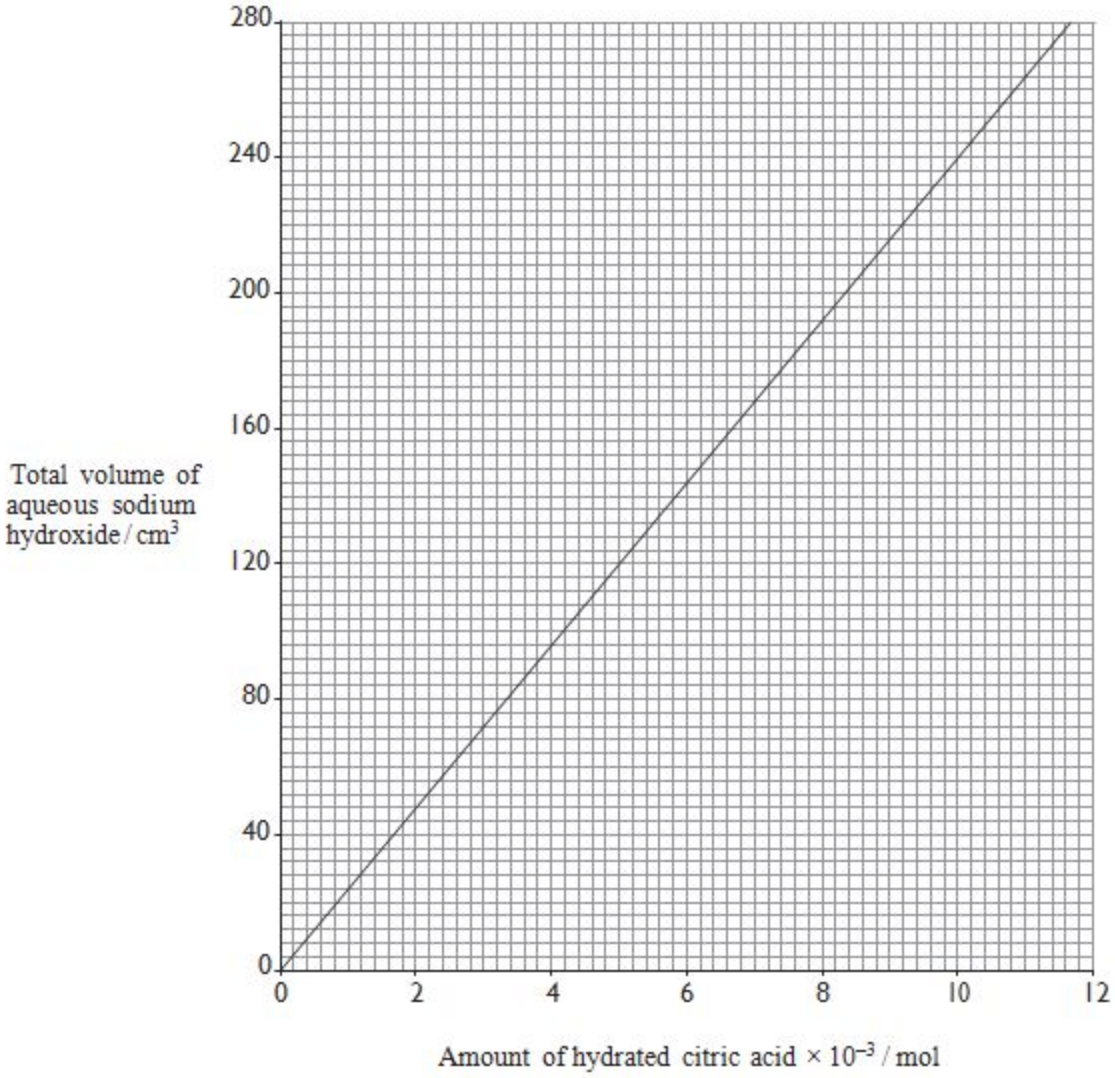
(b) Citric acid occurs in two forms – an anhydrous form and a hydrate.
Some students were given samples of the **hydrated** form of this tribasic acid and were asked to find its relative molecular mass by a titration with aqueous sodium hydroxide, using a suitable indicator to monitor complete neutralisation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

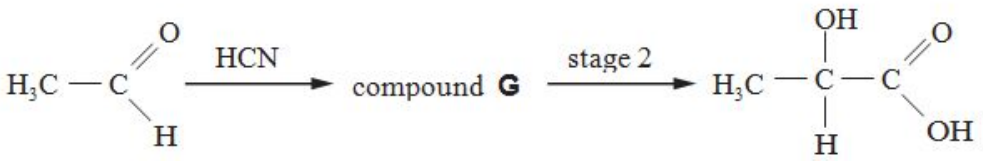
[1]

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

[1]

(Total 15)

5. *(a)* Lactic acid is a naturally-occurring compound that shows optical activity.
Lactic acid can be prepared from ethanal in the laboratory in a two stage process.



lactic acid

However, a sample prepared in this way was found to be optically inactive.

(i) Explain what is meant by a 'compound that shows optical activity'. [1]

(ii) Draw diagrams to show the two optical isomers of lactic acid

[1]

(iii) Give the displayed formula for compound **G.**

[1]

(iv) State the reagent(s) and condition(s) needed for stage 2.

[1]

(v) Explain why the sample prepared in the laboratory was optically inactive.

[2]

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

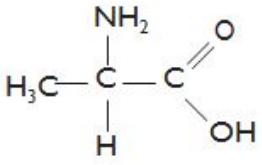
(i) sodium hydroxide,

[1]

(ii) acidified potassium dichromate.

[1]

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



compound *H*

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

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

[1]

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

[2]

(Total 12)

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

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

[1]

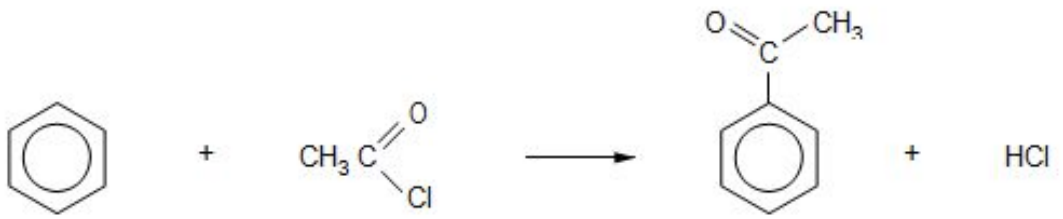
(ii) The free radical reaction of pentane with chlorine gives other chlorinated organic products. Give the structural formula of the carbon-containing free radical that leads to the formation of 2-chloropentane.

[1]

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

[1]

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



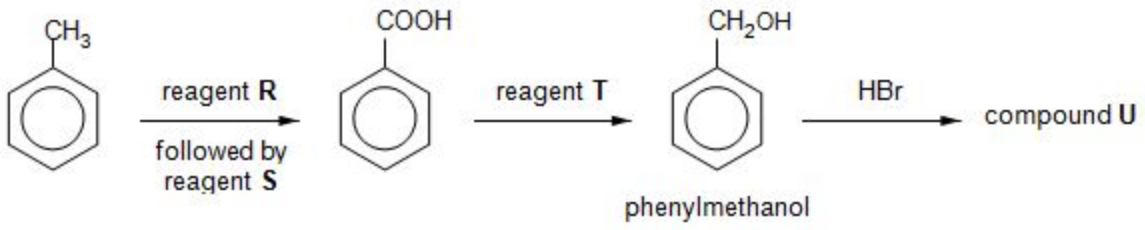
phenylethanone

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

[1]

(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]

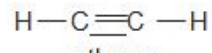
(Total 12)

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

Some chemistry of the alkynes

The alkynes are a homologous series of hydrocarbons, which have the general formula C_nH_{2n-2}.

The simplest member of the series is ethyne (acetylene). All alkynes contain a carbon to carbon triple bond (C≡C).

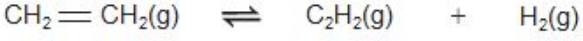


ethyne

Until 50 years ago ethyne was the main starting material for the preparation of aliphatic compounds. It was made by the reaction of calcium carbide with water.

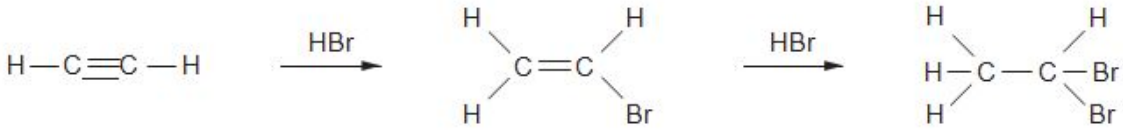


Since then the main source of organic compounds has been crude oil (petroleum).
A modern method for producing a good yield of ethyne is by heating ethene above 1150 °C.

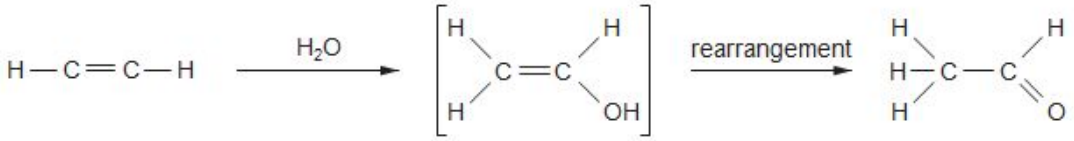


One laboratory method for making ethyne is by reacting 1,2-dibromoethane with an excess of alcoholic potassium hydroxide solution. Potassium bromide and water are the other products of this reaction.

Alkynes are unsaturated compounds and react similarly to alkenes when treated with a hydrogen halide.

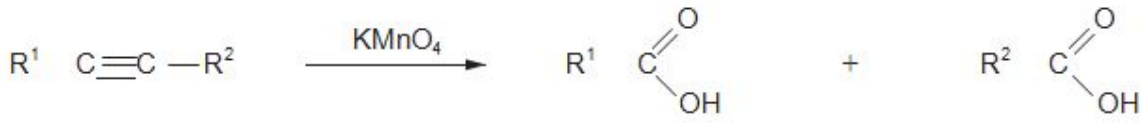


When ethyne is passed into aqueous sulfuric acid, containing mercury(II) ions as a catalyst, ethanal is produced.

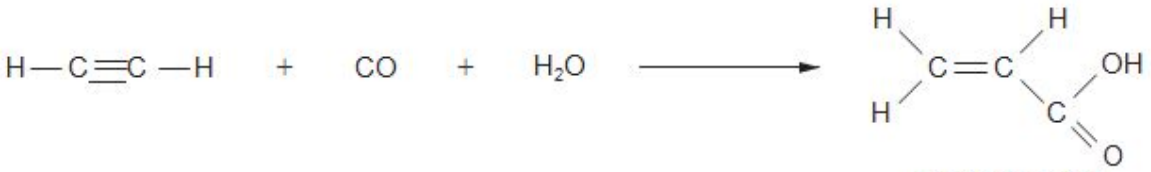


ethenol

The oxidation of ethyne to carbon dioxide and water is the chemical basis of oxy-acetylene welding. If an alkyne is less strongly oxidised by using potassium manganate(VII) solution under suitable conditions the C ≡C bond is broken to give carboxylic acids.



25 Complete carbon to carbon bond fission of the alkyne does not occur if the alkyne is reacted with carbon monoxide and water in the presence of a catalyst.



propenoic acid

- End of passage -

(a) Write the **displayed** formula of pent-2-yne.

[1]

(b) Chemical suppliers used to sell calcium carbide in tins containing 500 g. Calculate the volume of ethyne that will be obtained at room temperature and pressure from 500 g of calcium carbide (M_r 64.1) *(line 8)*.

[1 mol of ethyne has a volume of 24.0 dm^3 at room temperature and pressure] [2]

Volume = ... dm^3

(c) The article describes the preparation of ethyne from ethene *(lines 10-11)*. State how the information given indicates that this is an endothermic process.

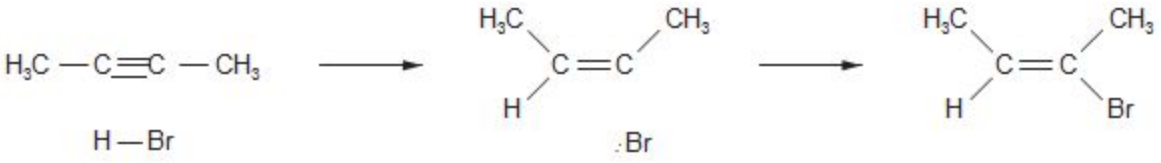
[1]

(d) Give the equation for the preparation of ethyne from 1,2-dibromoethane and potassium hydroxide solution *(lines 12-13)*

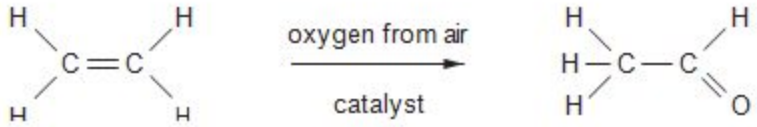
[1]

.

(e) Alkynes react with hydrogen bromide by electrophilic addition to give brominated alkenes. By analogy with the reaction of propene with hydrogen bromide, complete the mechanism of the reaction of but-2-yne with hydrogen bromide to give 2-bromobut-2-ene. [3]



(f) The article describes the preparation of ethanal from ethyne *(line 20)*. Another method uses ethene as the starting material.



Suggest **two** factors that should be considered when recommending which of these two processes should be used to produce ethanal. [2]

Factor 1.....

.....

Factor 2.....

.....

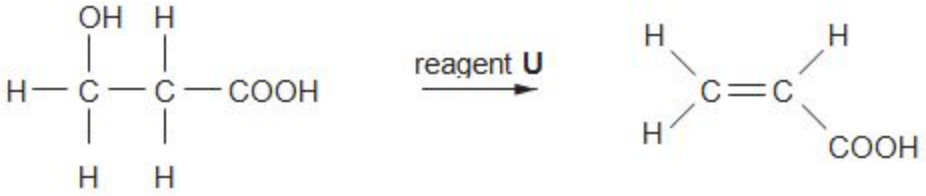
(g) Potassium manganate(VII) is used to break the —C≡C— triple bond to produce carboxylic acids. Give the displayed formula and hence the empirical formula of the alkyne that reacts in this way to give benzenecarboxylic acid and propanoic acid *(line 24)*. [2]

(h) Ethyne reacts with carbon monoxide in the presence of water to produce propenoic acid *(line 27)*.

(i) Give the structure of the repeating unit obtained when propenoic acid is polymerised to give poly(propenoic acid).

[1]

(ii) A new method to obtain propenoic acid is by the fermentation of a suitable sugar. This method gives 3-hydroxypropanoic acid, which can then be converted to propenoic acid.



3-hydroxypropanoic acid

I. Suggest the name of reagent **U**.

[1]

II. Use the data sheet to give a difference between the infrared spectrum of 3-hydroxypropanoic acid and propenoic acid

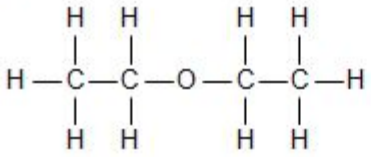
[1]

III. State why 3-hydroxypropanoic acid will **not** undergo the triiodomethane (iodoform) reaction. [1]

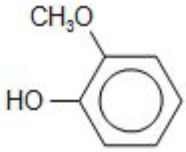
(Total 16)

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

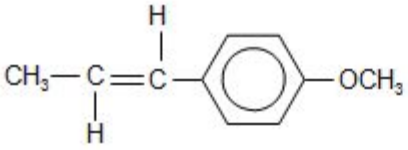
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C–O bond. Some examples are shown below.



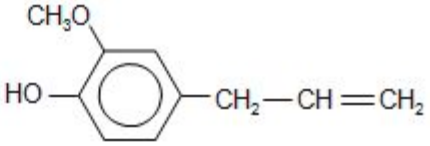
ethoxyethane



guaiacol

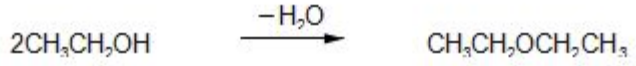


anethole



eugenol

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



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



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 -

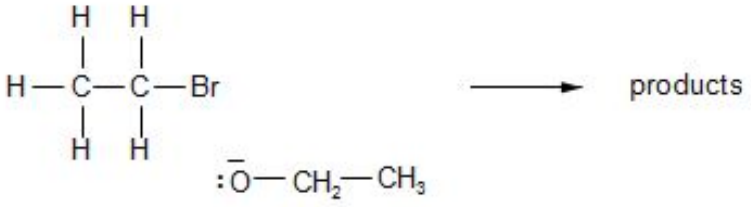
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol ($M_r = 46$) and obtained a 45 % yield of ethoxyethane ($M_r = 74$). Calculate the mass of ethoxyethane obtained. [3]

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.

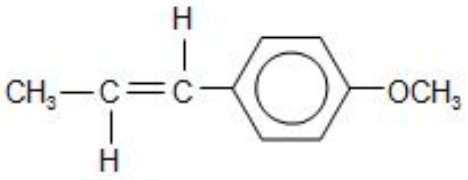
[2]

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]

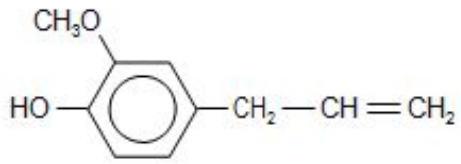


anethole

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]

9. *(a)* The formulae of some compounds are shown below.

$CH_3CH_2NH_2$	$CH_3CH_2CONH_2$	$CH_3CHCHCHO$
A	**B**	**C**
$CH_3CH(OH)CH_2CH_3$	CH_2CHCH_3	$CH_3CH_2COCH_2CH_3$
D	**E**	**F**

Each letter may be used once, more than once or not at all, to answer the questions below.

Give the letter of the compound which

(i) is most basic,

[1]

(ii) forms yellow crystals when warmed with iodine in alkaline solution,

[1]

(iii) forms a silver mirror when warmed with Tollens' reagent,

[1]

(iv) exhibits E-Z isomerism.

[1]

(b)(i) Butylamine is one of the compounds responsible for the smell of rotting fish. It can be prepared in the laboratory from 1-chlorobutane.

Classify the reaction mechanism when butylamine is prepared in this way

[1]

(ii) Explain why phenylamine, an aromatic amine, cannot be prepared from chlorobenzene using a similar reaction to that in part (i).

[2]

(iii) Write a **balanced** equation for the reaction of butylamine with ethanoyl chloride,

[1]

(iv) Phenylamine is normally prepared from nitrobenzene.

I. Give the reagents used in this preparation and a technique to separate the product from the reaction mixture.

[3]

II. When phenylamine reacts with cold nitric(III) acid (nitrous acid) a colourless solution of benzenediazonium chloride is formed. Write the formula for benzenediazonium chloride.

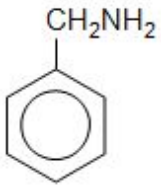
[1]

III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol.

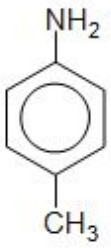
[1]

(Total 13)

10. *(a)* The formulae of the isomers phenylmethylamine and 4-methylphenylamine are shown below.



phenylmethylamine



4-methylphenylamine

These compounds are colourless liquids with different boiling temperatures.

(i) Give the name of a technique that can be used to separate these two liquids.

[1]

(ii) State and explain how the mass spectra of these two compounds would differ.

[1]

(iii) Phenylmethylamine reacts with ethanoyl chloride to give a white solid, compound **G**

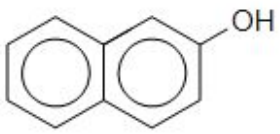
I. Give the equation for this reaction.

[1]

II. Compound **G** was purified by recrystallisation from ethanol. It has a melting temperature of 60 °C. Describe how you would recrystallise compound **G** from ethanol to obtain a pure dry product. You should assume that you are starting with cold ethanol and impure solid compound **G**. Washing of the purified solid product is unnecessary

[5] QWC [1]

(iv) 4-Methylphenylamine can be used to make an azo dye by reaction of its diazonium compound with an alkaline solution of naphthalene-2-ol.



naphthalene-2-ol

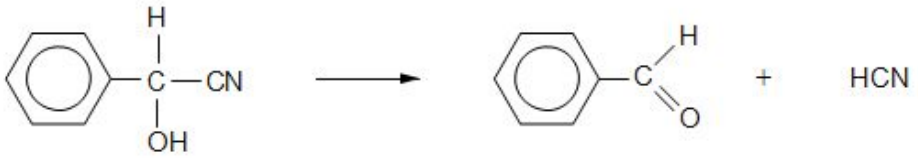
I. State how the diazonium compound can be made from 4-methylphenylamine, giving the reagents used and any essential conditions.

[2]

II. Give the structural formula of the azo dye produced.

[1]

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



2-phenyl-2-hydroxyethanenitrile (mandelonitrile)

benzaldehyde

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

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

[4]

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

[3]

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

[1]

(Total 20)

11.

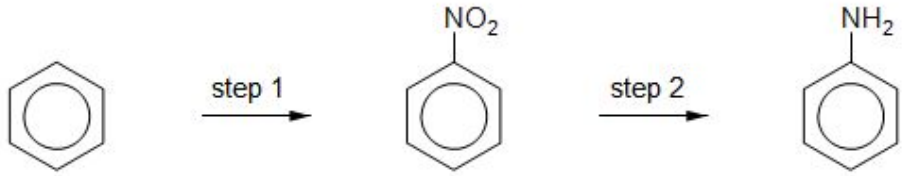
This question focuses on molecules that contain the $-NH_2$ group.

(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.

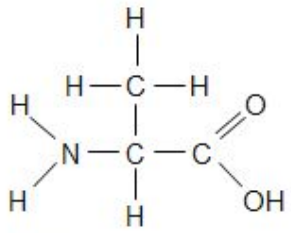
(i) Draw the **skeletal** formula for the molecule that would be combined with 1,6-diaminohexane to make Nylon-6,6

[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]

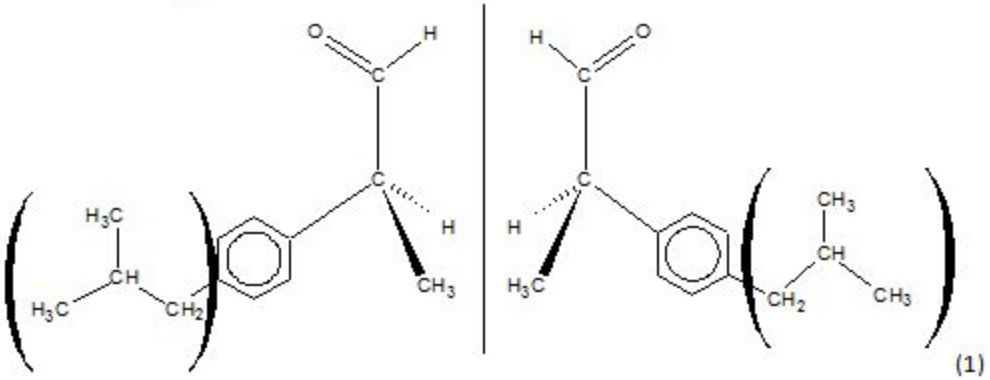
(Total 20)

2 (a) $CH_3CH(CH_3)CH_2Cl$ (1) $AlCl_3$ / $FeCl_3$ (1) Room temperature / in the dark (1) [3]

(b) (i) 2,4-DNP (1) Orange precipitate (1) [2]

(ii) Tollen's reagent (1) Silver mirror with **C**, no reaction with **B** (1) [2]

(c) Optical isomerism is where a molecule and its mirror image are different / non-superimposable (1)
Compound **C** has a chiral centre / 4 different groups attached to one carbon atom (1)



(1)

The two isomers rotate the plane of polarised light in opposite directions (1) [4]

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

(d) Dilute acid (1) heat (1) hydrolysis (1) [3]

(e) Acidified potassium dichromate (VI) (1) / heat (1)

One step reactions are generally better as they have a better yield / there is waste in each stage (1)

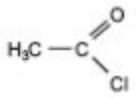
Two step process may be cheaper / use more sustainable reagents/ may give a better yield in this case / produce less harmful waste materials / potassium dichromate may react with other parts of the molecule as well / may be easier to separate product (1)

Do not credit same idea twice e.g. if 'better yield' gains first mark, a different point is required to gain second mark [4]

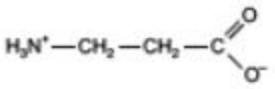
QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

Total [20]

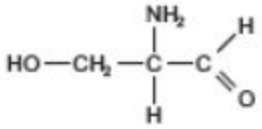
3 (a) (i) Sodium / potassium cyanide [1]

(ii)  [1]

(iii) Sulfuric / hydrochloric acid [1]

(iv)  [1]

(v) eg

 [1]

(vi) $LiAlH_4$ / H_2 / sodium, ethanol [1]

(vii) The nitrogen atoms act as electron pair donors / proton acceptors [1]

(b) (i) Molecular formula is $C_4H_4O_2$ [1]

(ii) 3 [1]

(iii) C = C / alkene [1]

(iv) Two of the (remaining) protons are in equivalent environments (and one is not) / there are CH and CH_2 present [1]

(v) Possibilities

 [1]

Total [12]

4 (a) (i) 48.5 / 49 % **[1]**

(ii) Find a use for the calcium sulfate **[1]**

(b) Total volume of aqueous sodium hydroxide needed = $\frac{26.40 \times 250}{25.00}$ = 264.0 cm^3 (1)

from the graph this is equivalent to 0.011 mole of the acid (1)

$\therefore M_r$ of the acid = $\frac{\text{mass}}{\text{no. of moles}} = \frac{2.31}{0.011} = 210$ (1)

$C_6H_8O_7 . n H_2O = 210$

192 $\therefore n = 18$ (1)

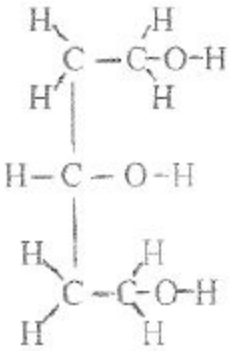
since M_r of water is 18 n = 1 (1) **[5]**

(c) The two 'ends' of the double bond have different groups bonded to the carbon atoms (of the double bond) / they have different structural formulae, so cannot be stereo / geometric isomers **[1]**

(d) eg sodium ethanoate / ethanoic acid (1) methane (1) **[2]**

(e) $C_5H_6O_5 \rightarrow CH_3COCH_3 + 2CO_2$ **[1]**

(f)



[1]

(g) (Fractional) distillation / (preparative) gas chromatography / HPLC **[1]**

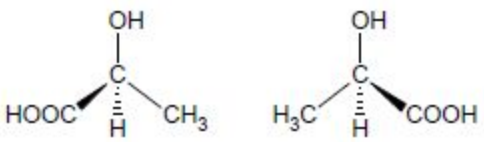
(h) (i) eg An optically active isomer that will rotate the plane of polarised light / an isomer with a chiral centre **[1]**

(ii) An equimolar mixture of both enantiomers (that has no apparent effect on the plane of polarised light) **[1]**

Total [15]

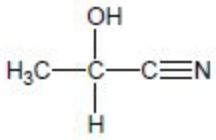
5 (a) (i) A compound that can rotate the plane of polarised light. [1]

(ii)



[1]

(iii)



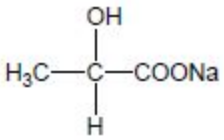
[1]

(iv) Reflux / heat with H_2O/H^+ [1]

(v) It contains an equal amount of the two enantiomers / it is a racemic mixture (1)

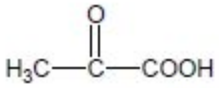
The rotating effect of one form exactly cancels out the effect of the other (1) [2]

(b) (i)



[1]

(ii)



[1]

(c) (i) 2-aminopropanoic acid [1]

(ii) Nitrous acid / nitric(III) acid / HNO_2 [1]

(iii) It exists as a zwitterion (1)

strong electrostatic attractions / ionic bonds between different zwitterions (1) [2]

Total [12]

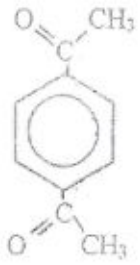
6 (a) (i) $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2CH_2CH_2Cl + HCl$ [1]

(ii) $CH_3CH_2CH_2\dot{C}HCH_3$ [1]

(b) (Anhydrous) aluminium chloride / iron(III) chloride allow $AlCl_3$ / $FeCl_3$ [1]

(c) (i) orange / red precipitate [1]

(ii)



(1) —$COCH_3$ groups in any positions

It must contain a C=O group but it is not an aldehyde as it does not react with Tollens' reagent (1) [2]

(d) (i) (Alkaline) potassium manganate(VII) (solution) allow $KMnO_4$ / MnO_4^- [1]

(ii) Dilute acid allow HCl / H^+ [1]

(iii) Lithium tetrahydridoaluminate(III) / lithium aluminium hydride
allow $LiAlH_4$ [1]

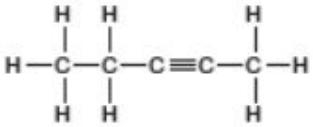
(iv)



(e) Only the infrared spectrum of benzoic acid would have a peak at 1650–1750 cm^{-1} (1)
This is due to the carbonyl group present in the benzoic acid (1) [2]

Total [12]

7 (a)



[1]

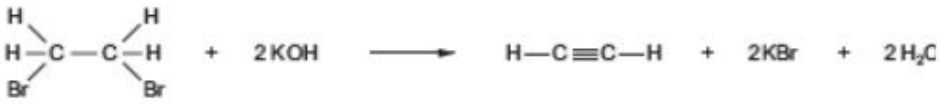
(b) Moles of calcium carbide = 500/64.1 = 7.80 (1)

Moles of ethyne = 7.80

Volume of ethyne = 7.80 × 24.0 = 187 (dm^3) (1) [2]

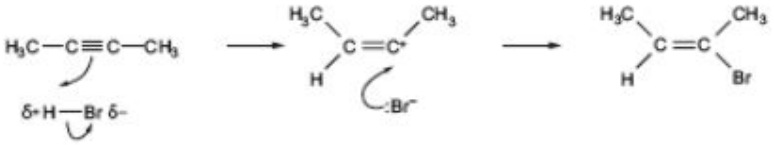
(c) If the process is endothermic left to right then it needs to absorb energy
– hence the high temperature / endothermic reactions need a high temperature [1]

(d)



[1]

(e)

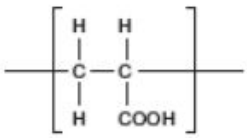


Curly arrows (1), full (1) and partial charges (1) [3]

(f) Any two for (1) each
energy costs / cost of **catalyst** / problems of separation of products / time taken / availability of starting materials / percentage yield / atom economy / relative health and safety [2]

(g) $C_6H_5 - C \equiv C - CH_2 - CH_3$ (1) C_1H_1 (1) [2]

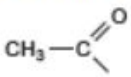
(h) (i)



[1]

(ii) I sulfuric acid / H_2SO_4 / phosphoric acid / H_3PO_4 / Al_2O_3 [1]

II 3-hydroxypropanoic acid does not show a C = C absorption at **1620–1670** cm^{-1} but this is present in propenoic acid [1]

III The  / $CH_3CH(OH)$ group is absent [1]

Total [16]

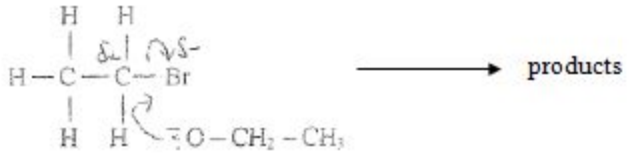
8 (a) (i) 2 mol of ethanol gives 1 mol of ethoxyethane (1)

Moles of ethanol = $\frac{69}{46}$ = 1.5

∴ Moles of ethoxyethane if theoretical yield = 0.75
∴ Moles of ethoxyethane if 45% yield = 0.75 × 0.45 = 0.34 (1)

Mass of ethoxyethane = 0.34 × 74 = 25g (1) allow error carried forward
[3]

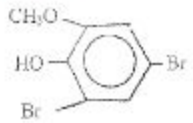
(ii) Ethene / C_2H_4 [1]

(iii) 

(1) for correct curly arrows (1) for correct δ^+ and δ^- [2]

(iv) They need to have an N–H / O–H / F–H bond / a highly electronegative atom bonded to hydrogen [1]

(b) (i) For example



[1]

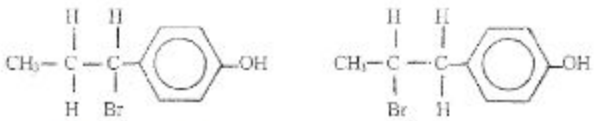
Accept any polybrominated species
Do not accept a monobrominated species

(ii) Bromine decolorised / orange to colourless / white solid [1]

(c) Reagent Iron(III) chloride solution / $FeCl_3$ (1)

Observation Purple coloration / solution (1) [2]

(d) (i) $C_{10}H_{12}O_1$ [1]

(ii) 

[1]

(e) Displayed formula, for example



(1)

Functional group carboxylic acid (1) [2]

Total [15]

9 (a) (i) **A** [1]

(ii) **D** [1]

(iii) C [1]

(iv) C [1]

(b) (i) Nucleophilic substitution [1]

(ii) The C–Cl bond in chlorobenzene is stronger than in 1-chlorobutane (1) due to delocalization of electron density from the ring with the bond (1)

OR

Delocalised electrons in chlorobenzene (1)
repel lone pair of electrons on nucleophile / ammonia (1)

[2]

(iii) $C_4H_9NH_2 + CH_3COCl \longrightarrow C_4H_9NHCOCH_3 + HCl$ [1]

(iv) I Tin and **concentrated** hydrochloric acid (1)

Add sodium hydroxide (after cooling) (1)

Steam distillation to separate the product (1) [3]

II $C_6H_5NN^+Cl^-$ [1]

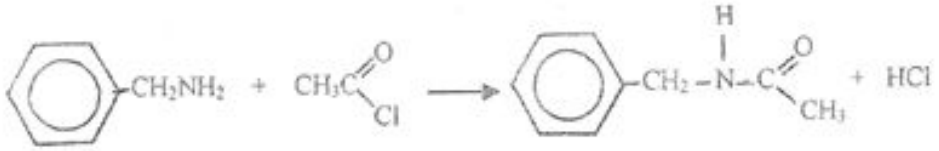
III Azo dye / azo compound [1]

Total [13]

10 (a) (i) (Fractional) distillation / (preparative) gas chromatography / HPLC / TLC column chromatography / solvent extraction [1]

(ii) the fragmentation pattern would be different / valid examples given [1]

(iii) I



[1]

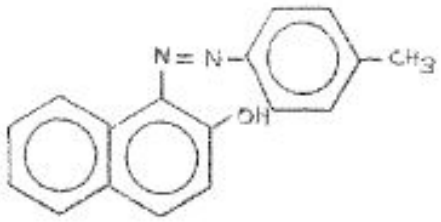
II Heated electrically / by a naked flame with a water bath (1)
Add compound **G** to the ethanol until the hot ethanol will (just) not dissolve any more solute (1)
Filter hot (1)
Allow to cool (1)
Filter (1)
Dry in air / window sill / < 60 °C in an oven (1) [5]

Maximum 4 out of 5 total if second marking point not given
Note 5 marks maximum here

QWC Information organised clearly and coherently, using specialist vocabulary where appropriate [1]

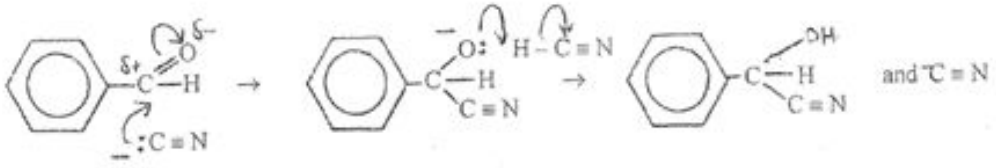
(iv) I The amine is reacted with sodium nitrite / HCl(aq) or nitrous acid (1)
at a temperature of < 10 °C (1) [2]

II



[1]

(b) (i) Nucleophilic addition (1)

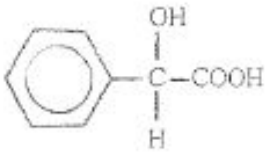


Accept a mechanism that shows HCN polarisation and nucleophilic addition as a concerted process

polarisation / charges shown (1) curly arrows on first structure (1)
regeneration of $^{-}C{\equiv}N$ or capture of H^{+} and curly arrow (1) [4]

(ii) Chromophores (1)
The colour will be black (1) as the compound absorbs blue / other colours (1)
[3]

(iii)



[1]

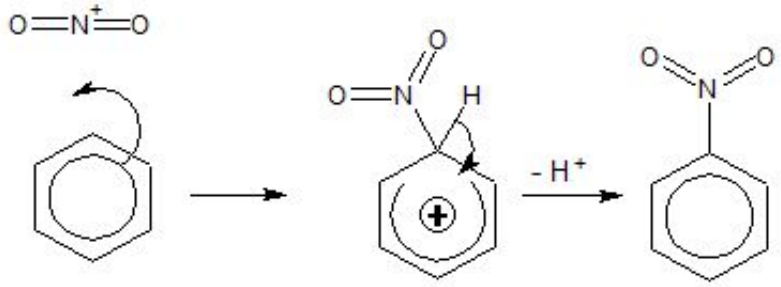
Total [20]

11 (a) (i) Both molecules have lone pairs on nitrogen (1)

The lone pairs can form (coordinate) bonds with H^+ ions (1) [2]

(ii) Lone pair on N in phenylamine is delocalised over benzene ring (1) therefore less able to accept H^+ (1) [2]

(iii) I Arrow in first step (1)
Cation structure in second step (1)
Arrow in second step (1)

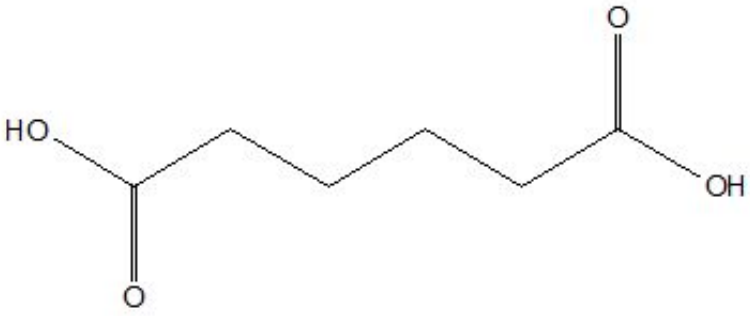


[3]

II (fractional) distillation / steam distillation [1]

III Sn and conc. HCl (1) followed by NaOH (1) [2]

(b) (i)



[1]

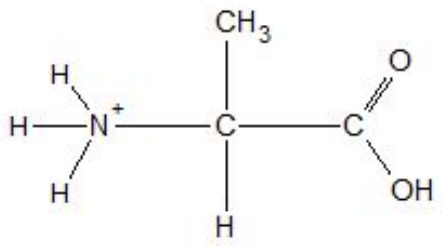
(ii) Addition polymerisation makes one product only /
Condensation produces one product plus a small molecule like water (1)

Addition polymerisation uses one starting material /
Condensation polymerisation has two different starting materials (1)

Addition polymerisation involves monomer with one functional group /
Condensation polymerisation involves monomer with two functional groups (1)

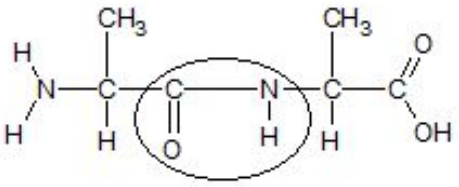
(max 2) [2]

(c) (i)



[1]

(ii)



[2]

(iii) Alanine has strong (electrostatic) forces between the zwitterions (1)

Butanoic acid has hydrogen bonding between molecules /
electrostatic forces in alanine are stronger than forces in butanoic acid (1)

[2]

(iv) Soda lime (1) $CH_3CH_2NH_2$ (1) [2]

Total [20]