Candidate Name	Centre Number	Candidate Number
		2

GCE A level

1094/01 **New A2**

Merged WJEC Paper 4s & Mark Schemes

January 2010 - June 2016

CHEMISTRY CH4

A.M. WEDNESDAY, 27 January 2010

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

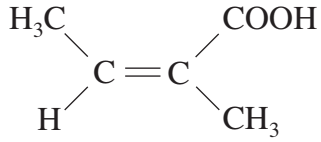
You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

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

1. *(a)* Angelic acid, (2-methylbut-2-enoic acid), is the traditional name for a compound produced by some plants as a defence against attack by beetles.



angelic acid

(i) This acid is one of a pair of stereoisomers.
Explain what is meant by the term stereoisomer. [1]

.....

.....

.....

(ii) Draw the **skeletal** formula of the **other** stereoisomer of angelic acid. [1]

(iii) The ethyl esters of these unsaturated acids have uses in the perfume industry.
State the reagent(s) and the condition(s), apart from heating, that are needed to produce ethyl angelate from angelic acid. [2]

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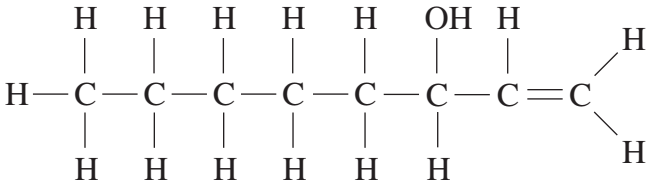
(b) Oct-1-en-3-ol, which shows optical isomerism, can be used as a mosquito repellent.



oct-1-en-3-ol

(i) Explain what is meant by a chiral centre. Indicate the location of a chiral centre on the formula above by using an asterisk (*). [2]

.....

.....

(ii) State how the two enantiomers of oct-1-en-3-ol affect the plane of polarised light. [1]

.....

(iii) State what is meant by a racemic mixture and how its solution would affect the plane of polarised light. [2]

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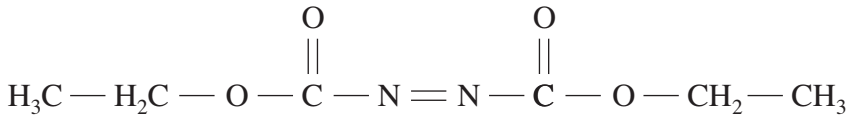
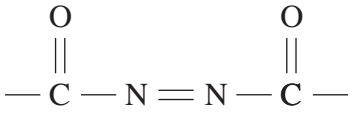
Examiner only

(c) Diethyl azodicarboxylate (abbreviated to DEAD)



is a shock-sensitive, toxic orange liquid.

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



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]

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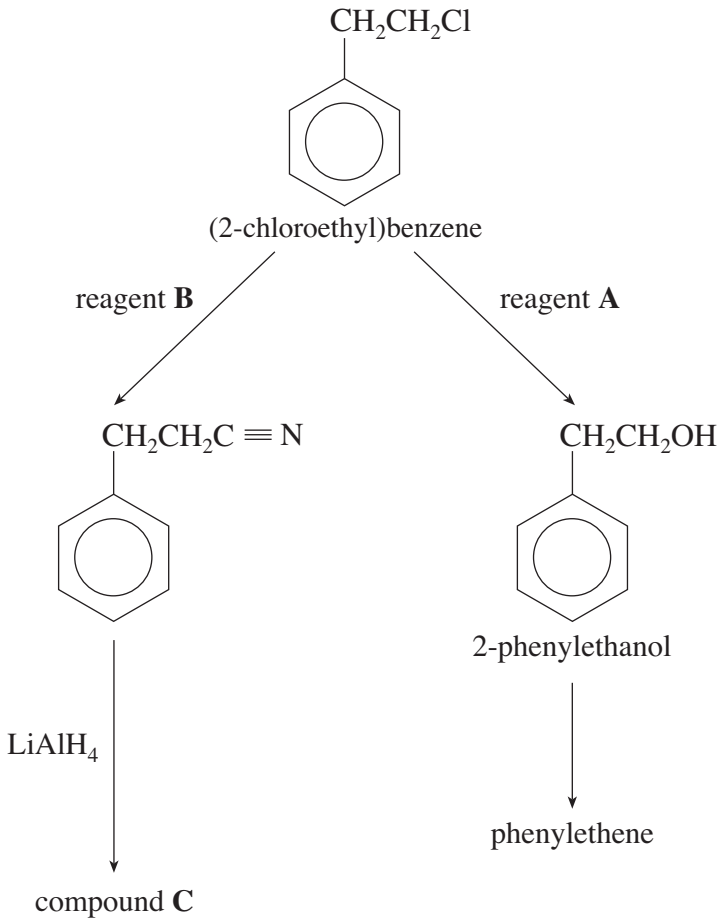
Total [13]

Examiner only

2. *(a)* (2-Chloroethyl)benzene is the starting material for the production of a number of other compounds.



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

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

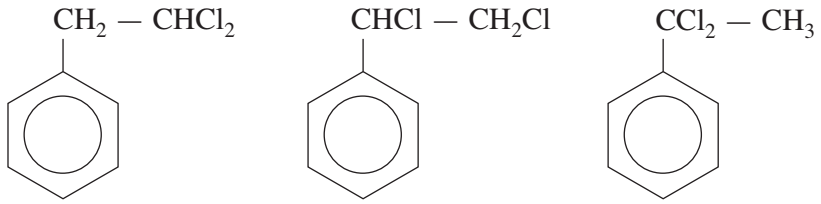
(iii) Name the type of reaction that occurs when phenylethene is produced from 2-phenylethanol. [1]

.....

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

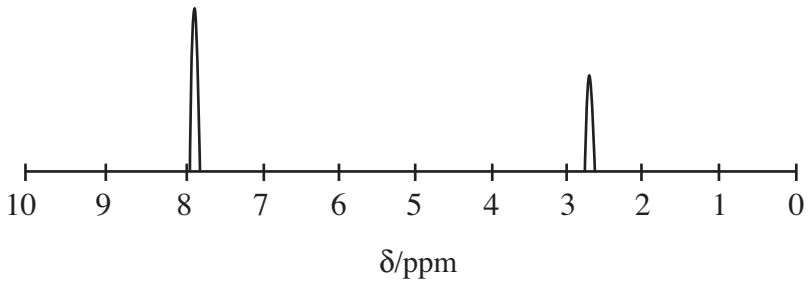
Examiner only

(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]

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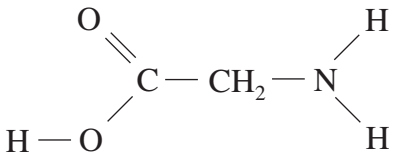
(c) (i) Aminoethanoic acid (glycine), whose displayed formula is shown below, reacts with ethanoyl chloride.



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

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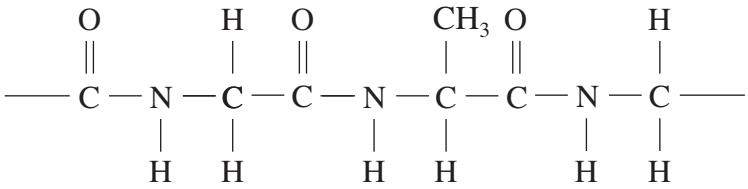
Examiner only

(ii) Draw the displayed formula of the zwitterion structure of aminoethanoic acid. [1]

(d) The formula of a section of a polypeptide is given below.



This formula represents the primary structure of a protein.

Briefly outline how the **secondary** structure of a protein arises from the primary structure. [2]

(QWC) [1]

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Total [12]

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

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

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

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

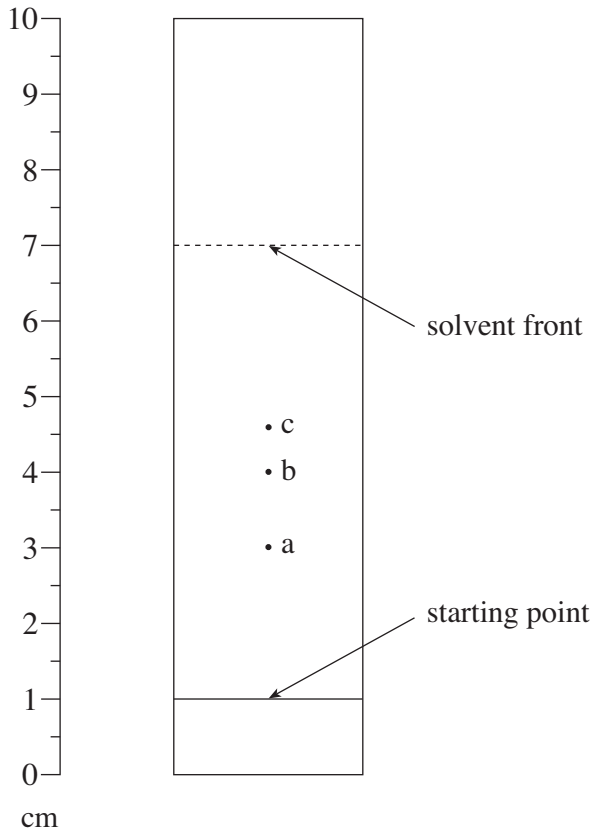
One industrial method for the production of ethanoic acid is to react methanol and carbon monoxide at a temperature of 450 K and a pressure of 30 atmospheres, in the presence of a suitable catalyst. The methanol and carbon monoxide have to be produced from coal, oil or natural gas. The process gives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

$$CH_3OH + CO \rightleftharpoons CH_3COOH$$

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

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

A typical TLC chromatogram is shown below.



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

- End of passage -

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

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

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

.....

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

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

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

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

Examiner only

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

(QWC) [1]

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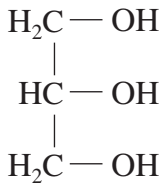
(c) The formulae of glycerol (propane-1,2,3-triol) and lauric acid (dodecanoic acid) are given below.



glycerol

$CH_3(CH_2)_{10}COOH$

lauric acid

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

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

Examiner only

(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]

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(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]

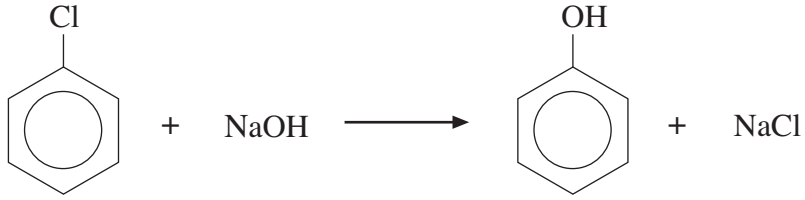
Section A Total [40]

SECTION B

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

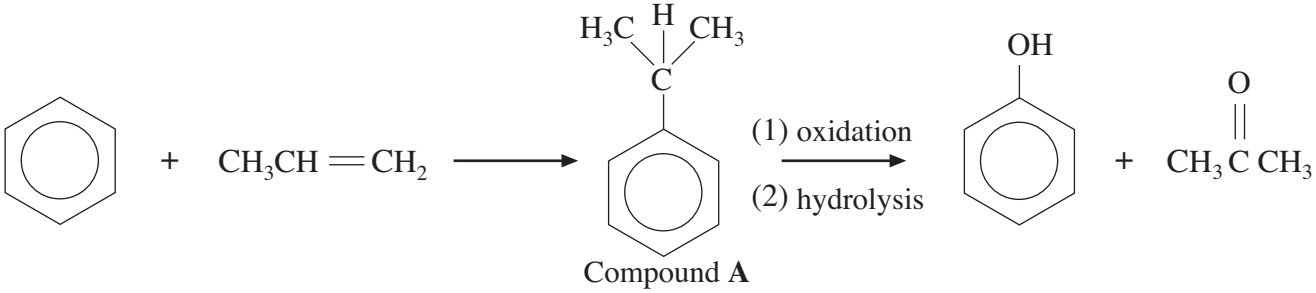
4. *(a)* Chlorobenzene, C_6H_5Cl, is an important industrial chemical. It can be made in the laboratory by reacting benzene and chlorine in the presence of an iron or iron(III) chloride catalyst.
Give the mechanism for this electrophilic substitution reaction. [4]

(b) One method for making phenol is by reacting chlorobenzene with aqueous sodium hydroxide, but at a pressure of 200 atmospheres.



Explain why it is difficult to react chlorobenzene with sodium hydroxide. [3]

(c) Most phenol is now produced from benzene and propene in a three-stage reaction.



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

(ii) Explain why the atom economy of this reaction to make phenol is poor. [2]

(iii) Using the Data Sheet, describe how an infrared spectrum of a sample of phenol produced in this process would indicate that traces of propanone were also present. [2]

(iv) At room temperature phenol is a solid. A sample of phenol was dissolved in ethanol and then a few drops of the solution were added to some iron(III) chloride solution. State what was seen and why ethanol is a suitable solvent to use for this reaction. [2]

(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]

5. *(a)* (i) Give an equation for the preparation of butylamine from a halogenoalkane. [1]

(ii) Discuss how the presence of the $-NH_2$ group in butylamine results in butylamine having a higher boiling temperature than expected for a molecule of this size. [4]

(iii) An aqueous solution of butylamine was tested using pH indicator/paper.
State the colour that was observed and **explain** why butylamine is able to cause this colour change. [3]

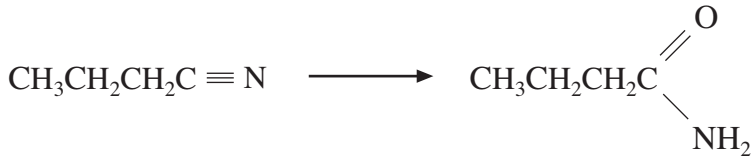
(b) Amides have important pharmacological and commercial uses and there is interest in the development of more economical production methods.

(i) In the past, the favoured method has been to heat the ammonium salts of carboxylic acids, for example ammonium butanoate gives butanamide.

$$CH_3CH_2CH_2COONH_4 \longrightarrow CH_3CH_2CH_2CONH_2 + H_2O$$

This is an energy-intensive process, which also gives small amounts of other products.
This makes the isolation of pure butanamide difficult.
In a pilot-scale experiment 50.0 kg of ammonium butanoate (M_r 105) was heated to produce 26.9 kg of butanamide (M_r 87).
Calculate the percentage yield of butanamide in this reaction. [3]

(ii) There is interest in developing processes that use less energy in production and separation, and that also give higher yields.
In one new biochemical experiment, researchers used an enzyme from a suitable bacterium to convert butanenitrile to butanamide.

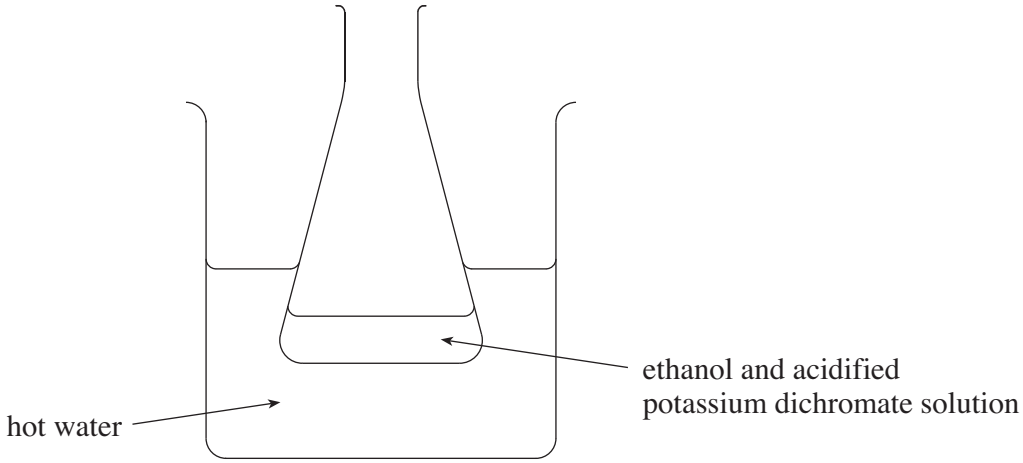


Details of the method
Temperature 10°C
Time taken 6 hours
Yield of butanamide > 99%

I Before publishing their results the researchers repeated their experiment.
State why this is an essential part of any research work. [1]

II If you were a member of the research team that discovered this new reaction, suggest what should be the next stage of research before proceeding to a larger scale trial. [1]

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



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

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

(QWC) [1]

Total [20]

Section B Total [40]

WJEC
CBAC

GCE MARKING SCHEME

CHEMISTRY (NEW)
AS/Advanced

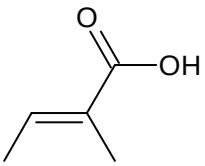
JANUARY 2010

CH4

SECTION A

1. (a) (i) Isomers whose atoms / groups take up different positions in space. [1]

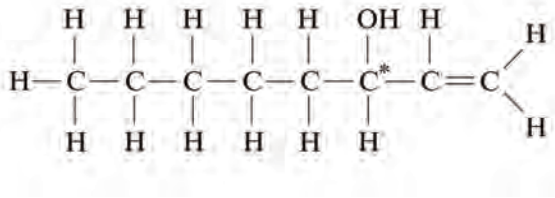
(ii)



[1]

(iii) Ethanol (1) in the presence of (concentrated) sulfuric acid / hydrogen chloride (acting as a catalyst). (1) [2]

(b) (i)



[1]

A carbon atoms that has four different groups / atoms bonded to it [1]

(ii) They rotate the plane of polarised light (in opposite directions) [1]

(iii) An equimolar / equal masses of the two enantiomers (1)

No (apparent) effect on the plane of polarised light (1) [2]

(c) (i) I Groups / atoms that are responsible for the absorption of (visible) light / giving colour [1]

II It absorbs 'blue' light / all other colours of the visible spectrum /transmits orange [1]

(ii) The CH_2 protons 'see' three protons on the adjacent CH_3 group and by the n+1 rule are split into a quartet. (1)
The CH_3 protons 'see' two protons on the adjacent CH_2 group and by the n+1 rule are split into a triplet. (1) [2]

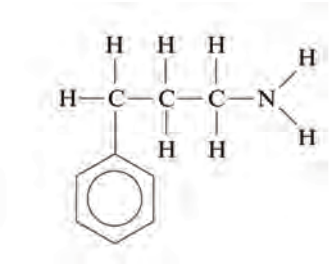
Total [13]

2. (a) (i) (Aqueous) sodium hydroxide – do not allow 'OH⁻' [1]

(ii) Potassium / sodium cyanide – do not allow 'CN⁻' [1]

(iii) Elimination / dehydration [1]

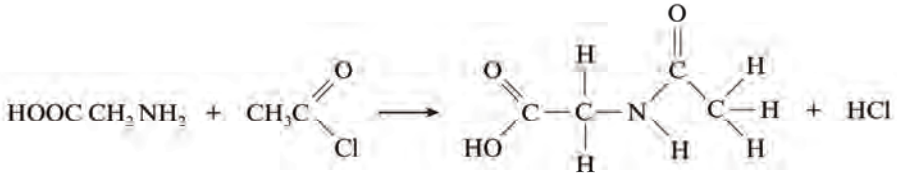
(iv)



[1]

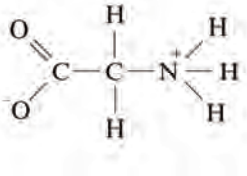
(b) Compound **T** (1); this has protons in only 'two' environments, ∴ 2 peaks (1) [2]

(c) (i)



balanced (1) correct displayed structure of ethanoyl derivative (1) [2]

(ii)



[1]

(d) The secondary structure results from hydrogen bonding (1). This occurs between the N – H and C = O groups of the polypeptide chain(s) (1) [2]

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

Total [12]

3. (a) (i) e.g. (Thorough) mixing of the solution [1]

(ii) Number of moles of

$$NaOH = \frac{26.25 \times 0.100}{1000} = 0.002625 / 2.625 \times 10^{-3}$$ (1)

Number of moles of CH_3COOH is also 0.002625 (1)

Concentration of the diluted solution

$$= \frac{1000 \times 0.002625}{25.00} = 0.105 \text{ mol dm}^{-3}$$ (1)

Concentration of the undiluted solution

$= 10 \times 0.105 = 1.05(0) \text{ mol dm}^{-3}$ (1) [4]

(b) Conditions although the temperatures are the same / moderate, method 2 needs higher pressures (1) (or vice versa)

Yield / Products Method 1 gives a higher yield / Method 2 gives a lower yield (1)
Method 1 gives few or no co-products / Method 2 gives a number of co-products (1)
The atom economy of the naphtha method is low (1)
There will be problems of the separation of products if method 2 is used (1)

- maximum 4 marks [4]

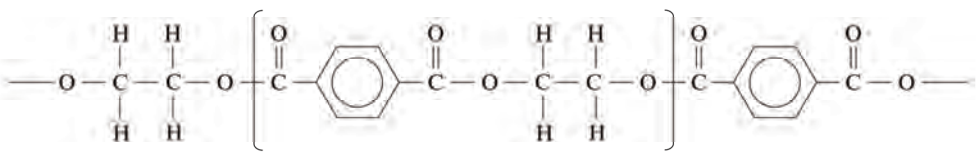
QWC Information organised clearly and coherently, using specialist vocabulary when appropriate [1]

(c) $CH_3(CH_2)_{10}COOCH_2$
|
$CH_3(CH_2)_{10}COOCH$
|
$CH_3(CH_2)_{10}COOCH_2$ [1]

(d) ethyl palmitate is **c** (1)

because $R_f = \frac{3.6}{6.0} = 0.60$ (1) [2]

(e)



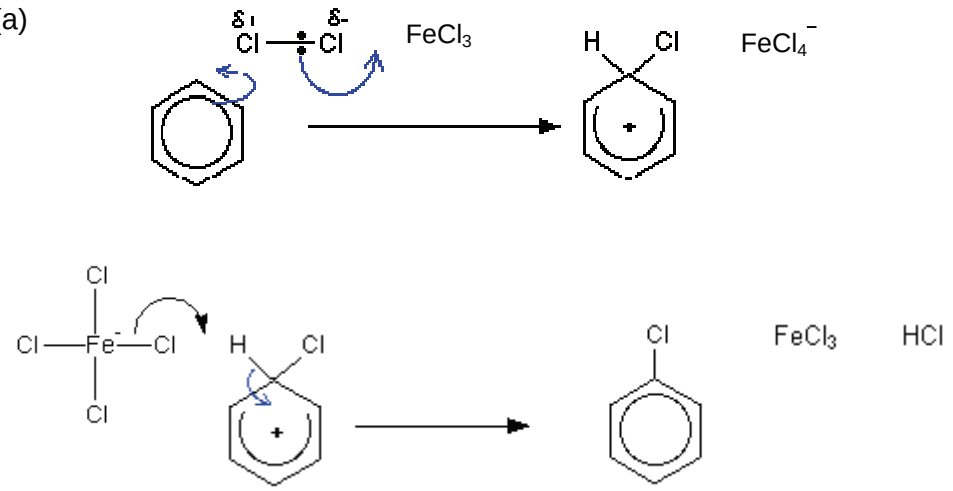
repeating unit (1) structure (1) [2]

Total [15]

Section A Total [40]

SECTION B

4. (a)



correct use of curly arrows (1)
polarisation of chlorine (1)
Wheland intermediate (1)
mechanism shows loss of H^+ or HCl (1)

[4]

(b) The chlorine lone pairs interact with the ring electrons (1)
strengthening the C – Cl bond / decreasing the C – Cl bond polarity (1)
making it less susceptible to nucleophilic attack (1) [3]

(c) (i) 2-propylbenzene / 2-phenylpropane / cumene [1]

(ii) Apart from phenol there is another product (1), the M_r of phenol and propanone are similar / OWTTE (1) [2]

(iii) Propanone would give a peak at ~ 1650 –1750 cm^{-1} (1)
due to the C = O bond (1) [2]

(iv) Purple colour / solution (1)
Ethanol does not react with $FeCl_3$ solution / ethanol is a polar solvent and will dissolve phenol / ethanol does not react with phenol (1) [2]

(v) An orange / red precipitate produced (1)
Melting temperature taken (1) and compared with literature value (1) [3]

(vi) $CH_3CH_2COCH_2CH_3$ M_r 86 (1)

$CH_3CH_2^+$ m/e 29 (1)

$CH_3CH_2CO^+$ m/e 57 (1)

Total [20]

5. (a) (i)

e.g. $CH_3CH_2CH_2CH_2Br + 2NH_3 \longrightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Br$ [1]

accept one mole of ammonia as a reactant and one mole of HX as a product

(ii) In the liquid phase butylamine molecules are attracted to each other (mainly) by hydrogen bonding (1). This is because the $-NH_2$ group is polar / correct mention of electronegativity / polarity shown in a diagram (1).
Attraction occurs between the nitrogen (lone pair) / (atom) of one molecule and the $\delta+$ hydrogen atom of another molecule (could be seen in a diagram) (1).
$\therefore$ stronger forces between molecules / more energy needed to separate molecules (and hence a higher boiling temperature). (1) [4]

(iii) The indicator turns blue / purple (1). This is because butylamine / amines are basic (1), as the lone pair on the nitrogen atom is a proton acceptor / or nitrogen is an electron pair donor (could be seen on a diagram) (1). [3]

(b) (i) 105 kg of ammonium butanoate gives 87 kg of butanamide
$\therefore$ 1 kg of ammonium butanoate gives $\frac{87}{105}$ kg of butanamide

$\therefore$ 50.0 kg of ammonium butanoate gives $\frac{87 \times 50.0}{105}$ kg of butanamide = 41.4 kg (1)

$$\% \text{ yield} = \frac{26.9 \times 100}{41.4} \quad (1) = 65 \ (1)$$ [3]

(ii) I To see if the results are reproducible. [1]

II See if the reaction time can be reduced. [1]

(c) (i) The (orange) mixture turns green (1) as the ethanol has reduced the acidified dichromate (to green Cr^{3+} (aq)). (1) [2]

(ii) Ethanol gives a mixture of ethanal (1) and ethanoic acid (1).
The ethanal present will give a silver mirror with Tollens' reagent (1)
The ethanoic acid present will fizz / effervesce / produce CO_2 when sodium hydrogencarbonate or carbonate is added (1) [4]
(Accept responses based on Fehlings' / Benedict's reagents, acidified dichromate, 2,4-dinitrophenylhydrazine and iodoform test.)

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

Total [20]

Section B Total [40]

Candidate Name	Centre Number	Candidate Number
		2

GCE A level

1094/01

CHEMISTRY CH4

A.M. WEDNESDAY, 26 January 2011

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1094 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

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 ..... .

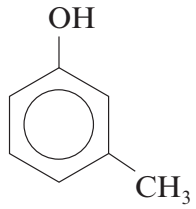
(b) Benzene reacts with chloromethane in the presence of a catalyst giving methylbenzene as the main organic product.

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

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

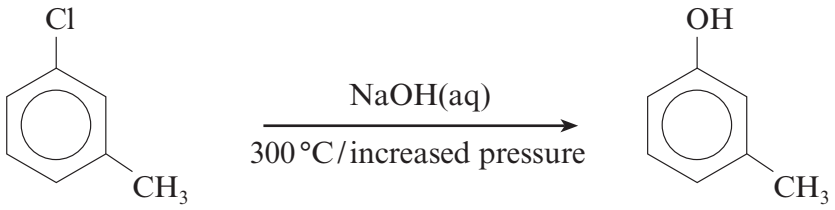
.....

(c) Creosote was once the most widely used wood preservative in the world. However, the use of this material is now severely restricted because of its high toxicity.
It is a mixture of compounds, including cresols such as 3-methylphenol.



3-methylphenol

(i) 3-Methylphenol is obtained from coal tar but another method of preparing this compound is by heating 3-chloro-1-methylbenzene with aqueous sodium hydroxide.



Explain why these conditions are needed to obtain 3-methylphenol from the chloro-compound. [3]

.....

.....

.....

.....

(ii) A number of safer wood preservatives have been developed to replace creosote.
Suggest **two** factors that companies should take into account, apart from toxicity and cost, when considering an alternative material for use as a wood preservative. [2]

1. .....

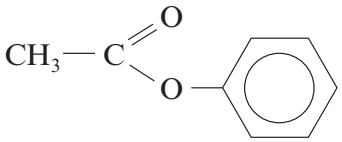
.....

2. .....

.....

Examiner only

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

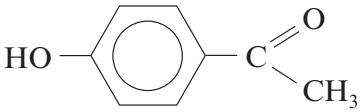


compound **W**

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

.....

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



compound **Y**

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

Reagents .....

Observation .....

Total [13]

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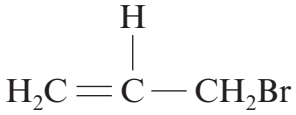
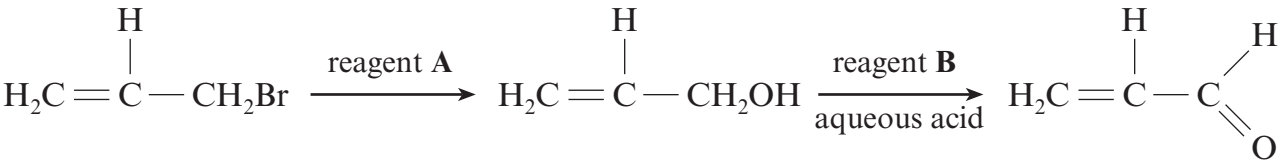
2. *(a)* Allyl bromide is the traditional name for the compound that has the following formula.



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

.....

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



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

Reagent **A** .....

Reagent **B** .....

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

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

.....

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

.....

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

.....

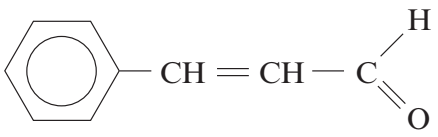
.....

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

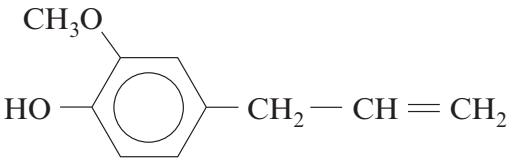
Displayed formula .....

Type of reaction .....

(c) The smell and flavour of cinnamon oil is largely due to cinnamaldehyde (3-phenylpropenal) and, to a smaller extent, eugenol.



cinnamaldehyde



eugenol

(i) Explain why only cinnamaldehyde, and not eugenol, is able to have E-Z isomers. [1]

.....

.....

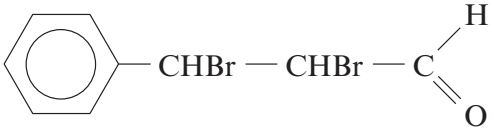
.....

(ii) Giving the reagent and an observation, state a chemical test that gives a positive result with eugenol but not with cinnamaldehyde. [2]

Reagent .....

Observation .....

(iii) Cinnamaldehyde reacts with bromine to give the chiral compound **C**.



compound **C**

Both compound **C** and cinnamaldehyde can be used to illustrate stereoisomerism. State what is meant by *stereoisomerism.* [1]

.....

.....

.....

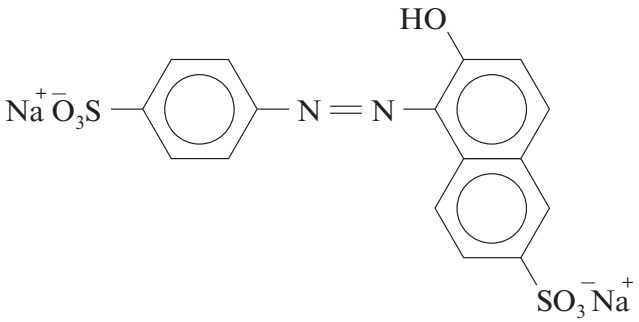
Total [12]

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.

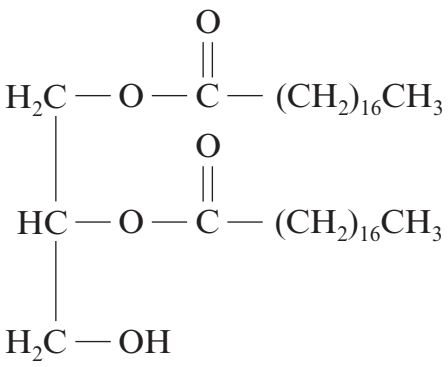
Colouring agents Consumers are probably most worried about compounds used to colour food. A number of permitted colours are synthetic azo-dyes and there are particular concerns about the effect that some of these compounds have on children. In recent years there has been a move towards safer naturally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



E110

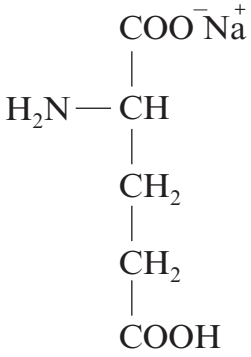
Preservatives With the move towards foods having longer shelf lives, there is a need to use preservatives to prevent spoilage. 2-Hydroxypropanoic acid (lactic acid), occurs naturally in sour milk and is used as a preservative in salad dressings. The salts of organic acids, for example sodium benzoate 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.



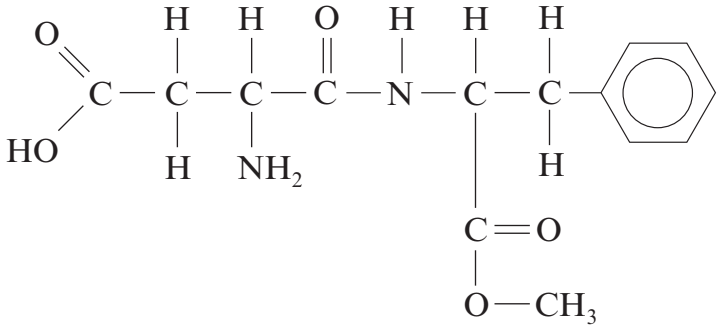
E477

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 –

Examiner only

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

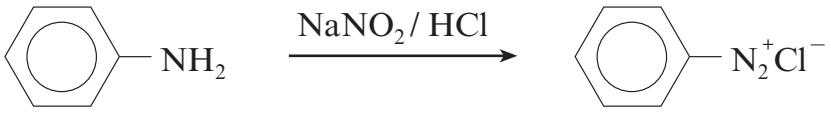
.....

(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]

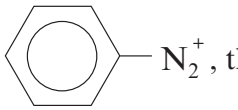
.....

.....

(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.

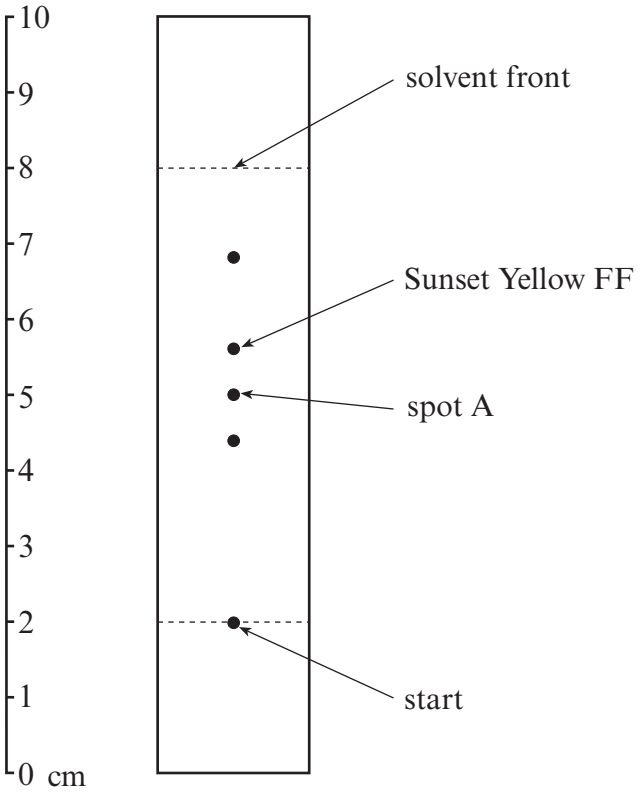
The benzenediazonium ion reacts as an electrophile.
State what is meant by the term *electrophile*. [1]

.....

.....

Examiner only

(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. .....

.....

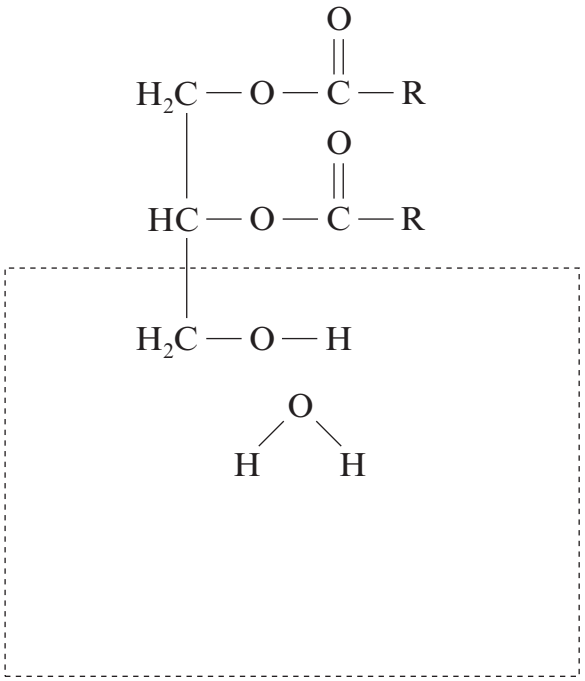
Examiner only

(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]

$(CH_3CH_2COO)_2Ca + Ca(OH)_2 \rightarrow \square\ CaCO_3 + \square$ .....

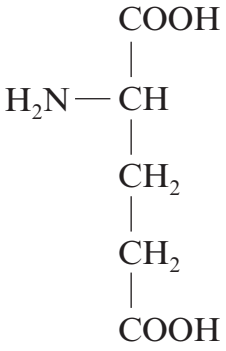
(d) E477 *(line 18)* forms hydrogen bonds with water molecules.

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]



Examiner only

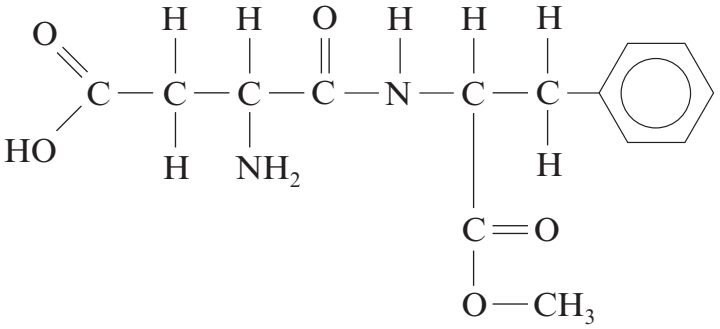
(e) MSG *(line 19)* is the monosodium salt of the α-amino acid glutamic acid.



glutamic acid

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

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



aspartame

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

Total [15]

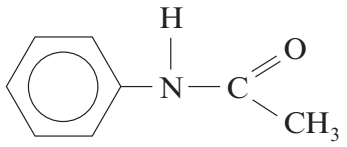
Section A Total [40]

Turn over.

SECTION B

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

4. *(a)* Phenylamine reacts with ethanoyl chloride to produce N-phenylethanamide.



These two reactants are mixed together under suitable conditions and the products are poured into a large excess of cold water, when N-phenylethanamide is formed as impure white crystals. After filtering, N-phenylethanamide is recrystallised from hot water. The pure product melts at 113 °C.

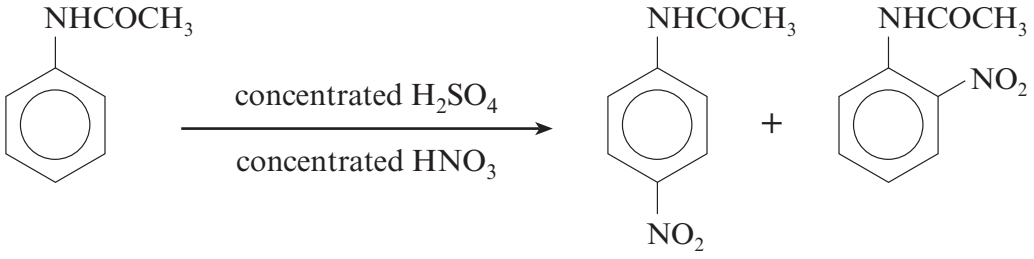
(i) Write the chemical equation for the reaction of phenylamine and ethanoyl chloride. [1]

(ii) When filtering the mixture containing impure N-phenylethanamide, the material in the filter paper is washed several times with cold water.
State why this is done. [1]

(iii) Use the account above to help you describe how you would obtain pure, dry crystals of N-phenylethanamide from the impure white crystals. [4]

(QWC) [1]

(b) N-phenylethanamide can be nitrated using a mixture of concentrated nitric and sulfuric acids, giving mainly 4-nitro-N-phenylethanamide as colourless crystals, together with small quantities of the yellow 2-nitro-N-phenylethanamide.



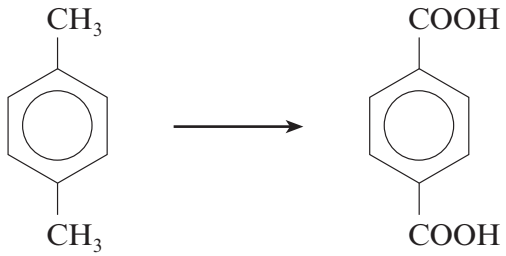
colourless solid yellow solid

(i) The mechanism for this reaction is similar to the nitration of benzene.
Give the reaction mechanism for the production of 4-nitro-N-phenylethanamide, starting from N-phenylethanamide and the nitronium ion (nitryl cation), NO_2^+.
Your answer should also state the type of reaction mechanism occurring. [4]

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

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

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



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

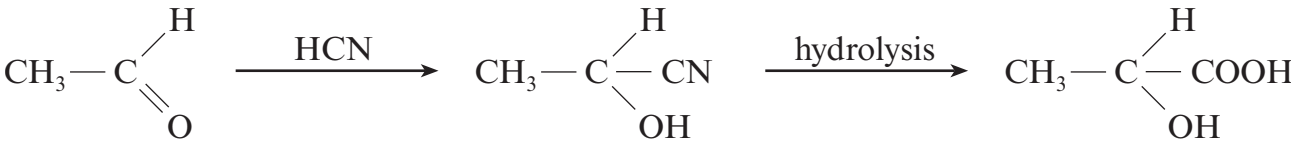
(i) State the name of oxidising agent **G**. [1]

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

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

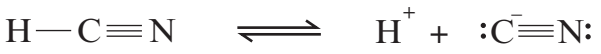
Total [20]

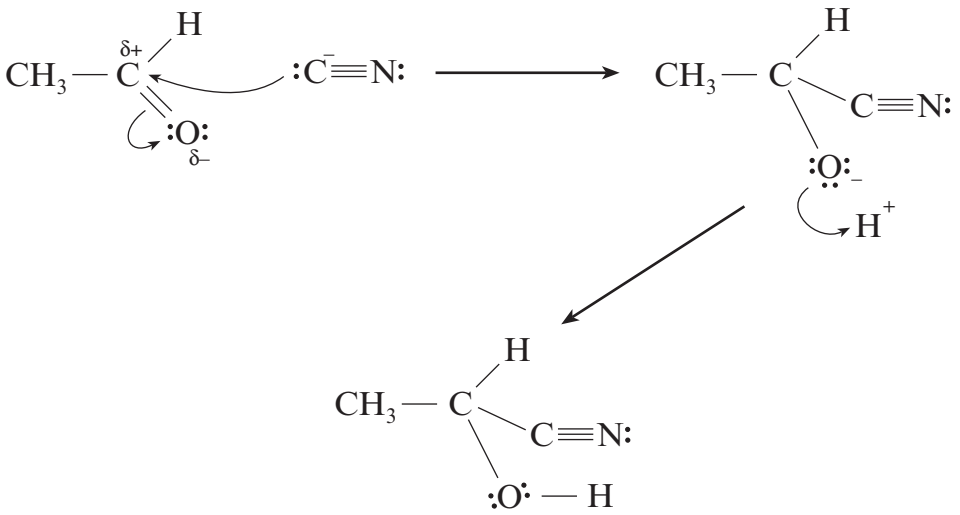
5. *(a)* 2-Hydroxypropanoic acid (lactic acid) can be made from ethanal by reaction with hydrogen cyanide and the subsequent hydrolysis of the 2-hydroxypropanenitrile.



2-hydroxypropanenitrile 2-hydroxypropanoic acid

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





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

(QWC) [1]

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

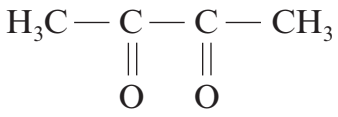
(b) (i) Yoghurt contains lactic acid that has been produced from lactose by certain bacteria.
The percentage of lactic acid in yoghurt can be found by an acid-base titration.
A sample of plain yoghurt of mass 50.0 g was titrated with sodium hydroxide solution of concentration 0.250 mol dm^{-3}. The lactic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

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

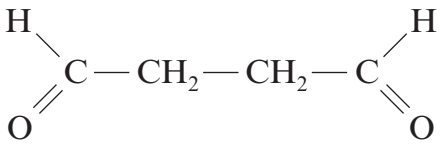
Use the information above and the equation to calculate the percentage of lactic acid present in the yoghurt. [3]

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

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



butan-2,3-dione



butan-1,4-dial

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

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

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

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

(QWC) [1]

Total [20]

Section B Total [40]

WJEC
CBAC

GCE A level

1094/01-A

CHEMISTRY CH4
DATA SHEET

A.M. WEDNESDAY, 26 January 2011

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C=C	1620 to 1670
C=O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

Period	1	2										3	4	5	6	7	0
	s Block													p Block			
1	1.01 H Hydrogen 1																4.00 He Helium 2
2	6.94 Li Lithium 3	9.01 Be Beryllium 4										10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12	d Block									27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	40.0 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98.9 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
6	133 Cs Caesium 55	137 Ba Barium 56	139 ▶ La Lanthanum 57	179 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86
7	(223) Fr Francium 87	(226) Ra Radium 88	(227) ▶▶ Ac Actinium 89															

Key

A_r Symbol Name Z — relative atomic mass; atomic number

f Block

▶ Lanthanoid elements	140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	(153) Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
▶▶ Actinoid elements	232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103

GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

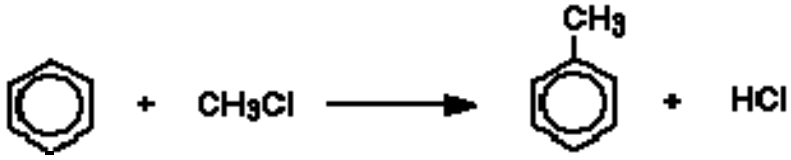
JANUARY 2011

CH4

SECTION A

1. (a) (i) $C_6H_5NO_2$ (1)
the blue light is absorbed / there is no yellow light to be reflected / transmitted (1)
equivalent (1) [3]

(b) (i)



[1]

(ii) aluminium chloride / iron(III) chloride / correct formulae [1]

(c) (i) The chlorine's (lone pair of) electrons interact with the ring π cloud of electrons (1)
making it less polar / stronger bond (1)
and therefore less susceptible to **nucleophilic** substitution (1) [3]

(ii) Any TWO from
e.g. ease of manufacture / availability of starting materials / percentage yield / shelf life of product / life of product in use / effectiveness / suitability / range of colours [2]

(d) (i) esters [1]

(ii) reagents iodine / sodium hydroxide
OR sodium chlorate(I) / potassium iodide
I_2 / NaOH or OH^- NaClO / ClO^- / KI / I^- (1)

observation **yellow** precipitate / solid / crystals (1)
(antiseptic smell is a neutral answer) [2]

Total [13]

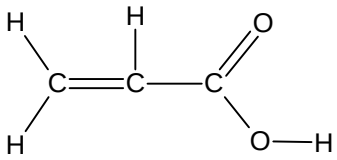
2. (a) (i) 3-bromopropene/3-bromoprop-1-ene [1]

(ii) Reagent A (aqueous) sodium hydroxide / NaOH / OH^- (1)
Reagent B potassium dichromate / $K_2Cr_2O_7$ / $Cr_2O_7^{2-}$ (1) [2]

(b) (i) condensation / (nucleophilic) addition – elimination [1]

(ii) red / yellow / orange solid (a solid must be implied) [1]

(iii) take its melting temperature, compare this with known values [1]

(iv) Displayed formula  [1]

Type of reaction oxidation / redox [1]

(c) (i) Both carbon atoms of the double bond need to have different atoms / groups attached to them [1]

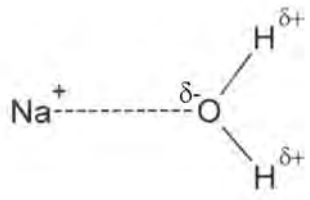
(ii) Reagent iron(III) chloride / $FeCl_3$ OR aqueous bromine (1)
Observation purple/blue/green colour white precipitate (1) [2]

(iii) It is shown by compounds that have the same structural formula but where their bonds take up different positions in space [1]

(do not accept descriptions of geometrical/optical isomerism)

Total [12]

3. (a) (i) Chromophore [1]

(ii) 

The sodium ions are attracted to the δ- oxygen atom of a water molecule [1]

(iii) I 0 - 10 ^oC / <10°C [1]

II (An ion that is) an electron **pair** acceptor / seeks out an electron rich site [1]

(accept an electron deficient group/species)

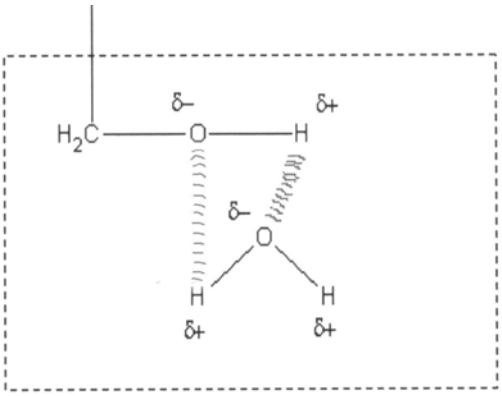
(b) (i) Brilliant Blue FF (1) as it has R_f value 0.80 and this has been identified on the chromatogram (1) [2]
must have the correct deduction, either 2 or 0 here

(ii) Any TWO from e.g.
repeat the chromatography using a different solvent / take its visible spectrum and compare its λ_{max} with those of the two dyes / take its infrared spectrum and compare with the spectrum of the two dyes / take its NMR spectrum and compare its spectrum with the NMR spectrum of each individual dye (1), (1) [2]

(c) $(CH_3CH_2COO)_2Ca + Ca(OH)_2 \rightarrow \mathbf{2}\ CaCO_3 + \mathbf{2}\ C_2H_6$

correct balancing (1) correct formula of ethane (1) [2]

(d)

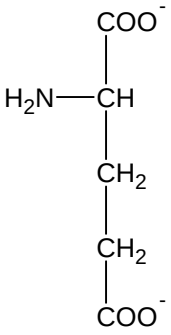


polarisation (1)

hydrogen bonding (1)

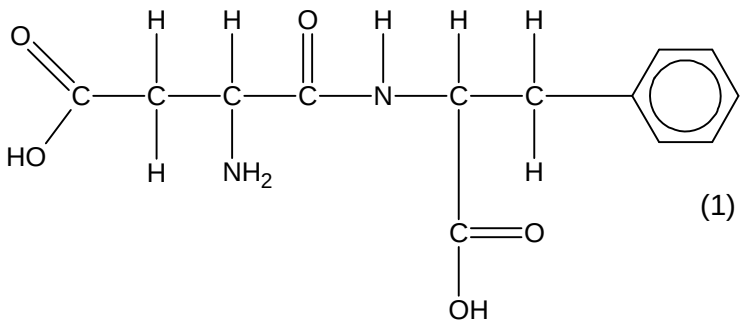
[2]

(e)



accept the formula with Na^+ ions [1]

(f)



(1)

+ CH_3OH (1)

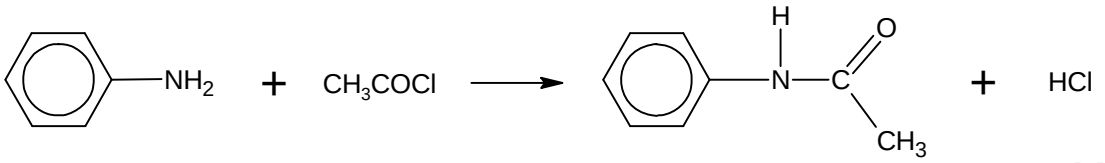
[2]

Total [15]

Section A Total [40]

SECTION B

4. (a) (i)



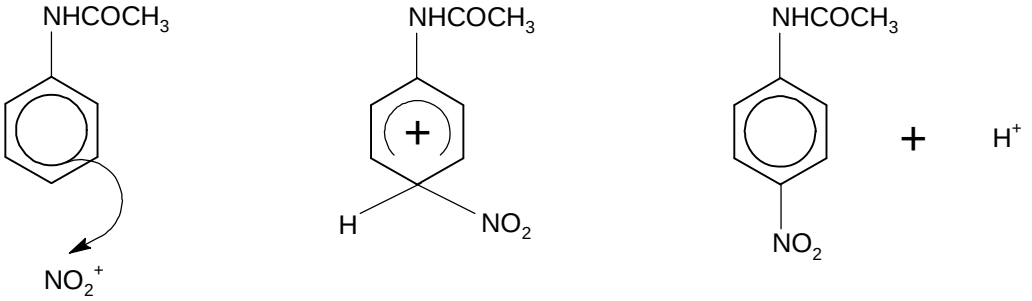
[1]

(ii) To remove **soluble** impurities [1]

(iii) The impure crystals are added to the **minimum** quantity of **hot water** / added to sufficient cold water and heated until all the crystals just dissolve / OWTTE (1) filter hot (1)
Allow the mixture to cool (1)
The product is then filtered (1) (washed) and dried in an oven at a **temperature <113 °C** / accept other drying methods that imply the temperature is <113 °C (1) [4]

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

(b) (i)



(1) (1) (Wheland) intermediate (1) products

electrophilic substitution (1) [4]

(ii) Since the 2-isomer is yellow (1) and the 4-isomer is colourless; when the 4-isomer is colourless / 'not yellow' then the 4-isomer is no longer contaminated (1) [2]

(iii) Moles of N-phenylethanamide $= \frac{8.10}{135} = 0.060$ (1)

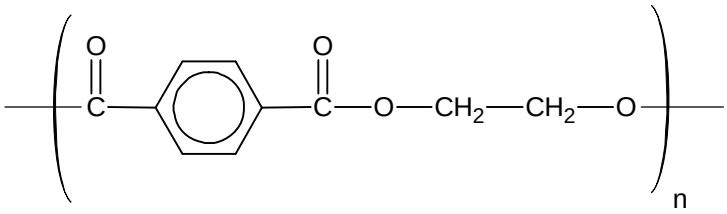
Moles of the 4-isomer $= \frac{6.48}{180} = 0.036$ (1)

% Yield $= \frac{0.036 \times 100}{0.060} = 60.(0)$ (1)

[3]

(c) (i) Potassium manganate(VII) / permanganate / $KMn0_4$ [1]

(ii) To convert the (sodium) salt back to the (parent) acid [1]

(d) 

(1)

in condensation polymerisation a small molecule / water is lost / produced (1)
[2]

Total [20]

5. (a) (i) Hydrogen cyanide ionises/dissociates (giving a hydrogen ion / H^+ and a cyanide ion / CN^-) (1)
(The mechanism is described as nucleophilic addition) because the CN^- ion acts as a nucleophile / base / electron pair donor (attacking (accept 'approaches') a δ+ site) (1)
Electron density increases / negative charge produced on the oxygen atom (1)
This oxygen atom acts as an electron pair donor, attracting a hydrogen ion (1)
In effect a molecule of hydrogen cyanide has added across the carbon to oxygen double bond (1)
(Accept any four correct points) [4]

QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning [1]

(ii) Hydrolysis is a reaction with water (or a water containing reagent), where water 'splits' the 'organic molecule (1)
In this reaction, hydrochloric / (dilute) sulfuric acid is used (1) [2]

(b) (i) Number of moles of sodium hydroxide $= \frac{20.00 \times 0.250}{1000} = 0.005$ (1)

Number of moles of lactic acid = 0.005

Mass of lactic acid = 0.005 x 90 = 0.45 g (1)

Percentage of lactic acid in the yoghurt $= \frac{0.45 \times 100}{50} = 0.90$ (1) [3]

(ii) It would produce a much smaller titre and this will lead to larger % errors - both statements required [1]

(c) The dione does not react with Fehling's reagent (1)
The dial produces a brown solid (1) [2]

(d) Molecular formula must be $\frac{172}{43} = 4$ ∴ $C_8H_{12}O_4$ (1)

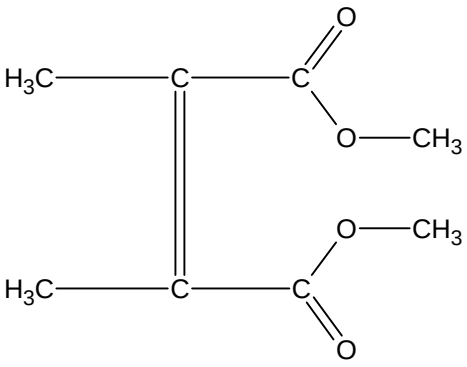
All oxygen atoms in ester group(s) - each ester group needs two oxygen atoms
∴ 2 ester groups (1)

Decolourises aqueous bromine ∴ $C{=}C$ (1)

Gives methanol as the only alcohol on hydrolysis ∴ methyl ester (1)

^{1}H NMR suggests each signal ≡ 6 protons, 'remotely bonded' (1)

Ester is



(1)

[6]

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

Total [20]

Section B Total [40]

Surname	Centre Number	Candidate Number
Other Names		2

WJEC CBAC

GCE A level

1094/01

CHEMISTRY CH4

P.M. THURSDAY, 26 January 2012

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1094 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

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

1. *(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]

.....

.....

.....

.....

Examiner only

(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]

1094 010003

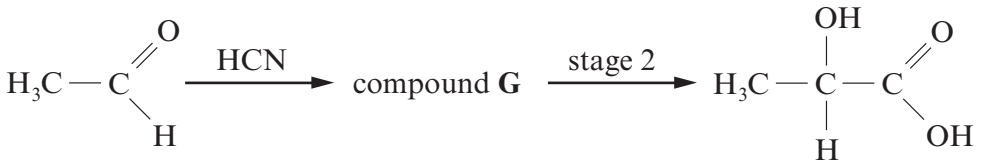
III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol. [1]

.....

Total [13]

Examiner only

2. *(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]

.....

.....

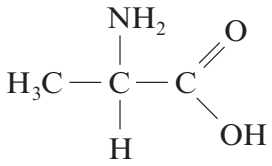
.....

(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]

.....

.....

.....

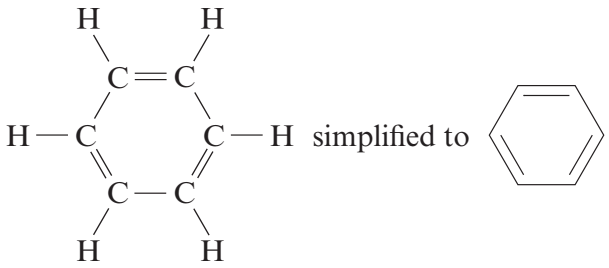
Total [12]

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

Benzene

Benzene, C_6H_6, is a colourless, highly flammable liquid with a sweet smell, but it is carcinogenic. The word "benzene" derives historically from "gum benzoin", an aromatic resin known to European pharmacists and perfumers since the 15th century.

Discovering the structure of benzene proved to be quite difficult. Benzene was first isolated and identified by Michael Faraday in 1825 from the oily residue derived from the production of illuminating gas. However, it was not until 1865 that Kekulé proposed this structure for benzene.

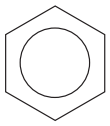


However this structure fails to explain why benzene does not react like an alkene. Ethene reacts readily with bromine as follows:

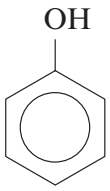
$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br\,CH_2Br$$

In contrast, benzene needs far more stringent conditions to react with bromine.

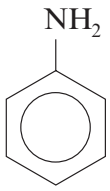
It was around 1930 that the structure of the benzene ring was finally confirmed using X-ray diffraction. It was shown that all the carbon-carbon bonds were of the same length. To account for this, it was proposed that three pairs of electrons were not localised in particular double bonds, but were shared equally amongst all six carbons. These electrons were said to be delocalised giving benzene great stability (delocalisation energy of benzene). The structure of benzene is therefore usually represented as:



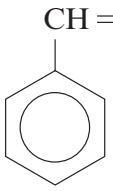
An understanding of the structure of benzene was crucial to early chemists since benzene is the parent molecule of all arene or 'aromatic' compounds and a huge variety of compounds are derived from benzene. Simple benzene derivatives include:



phenol



phenylamine

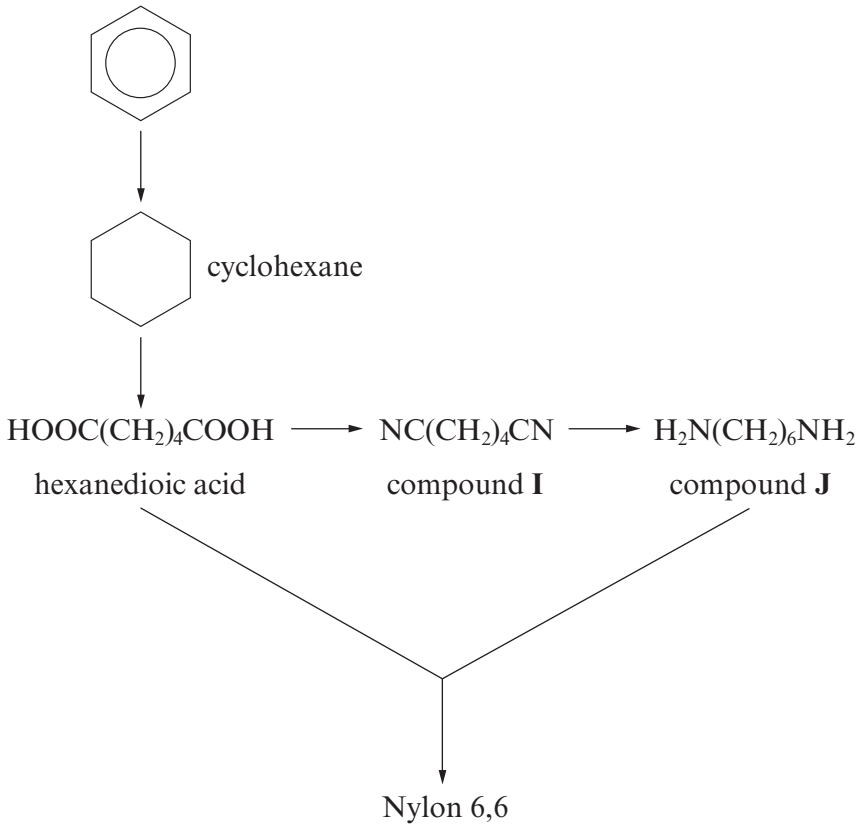


phenylethene

In the 19th and early 20th centuries, benzene was used as an after-shave lotion because of its pleasant smell, but today benzene is used to make other chemicals.

Examiner only

One of its most widely-produced derivatives is cyclohexane, which is used in the manufacture of Nylon 6,6 as shown in the scheme below:



28

– End of passage –

(a) Benzene reacts with bromine *(line 12)* in the presence of an iron(III) bromide catalyst to form bromobenzene.

(i) Classify the reaction mechanism. [1]

.....

(ii) Draw the mechanism for this reaction. [3]
(The mechanism is similar to that for the chlorination of benzene.)

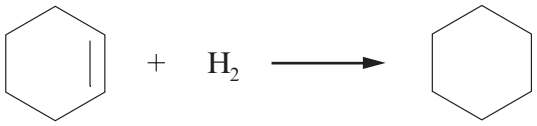
(b) (i) Explain what is meant by the *delocalisation energy* of benzene *(line 17)*. [1]

.....

.....

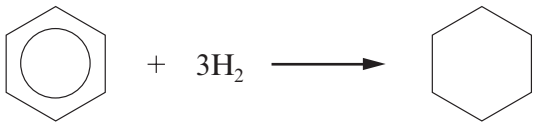
.....

(ii) Given that the enthalpy change of hydrogenation of cyclohexene is $-120\,kJ\,mol^{-1}$ and that the enthalpy change of hydrogenation of benzene is $-208\,kJ\,mol^{-1}$, calculate the delocalisation energy of benzene. [2]



$\Delta H^{\ominus} = -120\,kJ\,mol^{-1}$

cyclohexane



$\Delta H^{\ominus} = -208\,kJ\,mol^{-1}$

benzene

.....

.....

.....

$\Delta H^{\ominus}$ = ... $kJ\,mol^{-1}$

(c) Use the information in the passage to give a reason why benzene is no longer used in after-shave lotion. [1]

.....

(d) In the production of Nylon 6,6 *(line 28)* each of the repeating units requires **two** molecules of benzene; one for the formation of hexanedioic acid and one for the formation of compound **J**.

(i) Draw the **skeletal** formula of hexanedioic acid. [1]

(ii) Name the type of reaction occurring when compound **I** is converted to compound **J**. [1]

.....

(iii) State the name of compound **J**. [1]

.....

Examiner only

(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]

.....

.....

.....

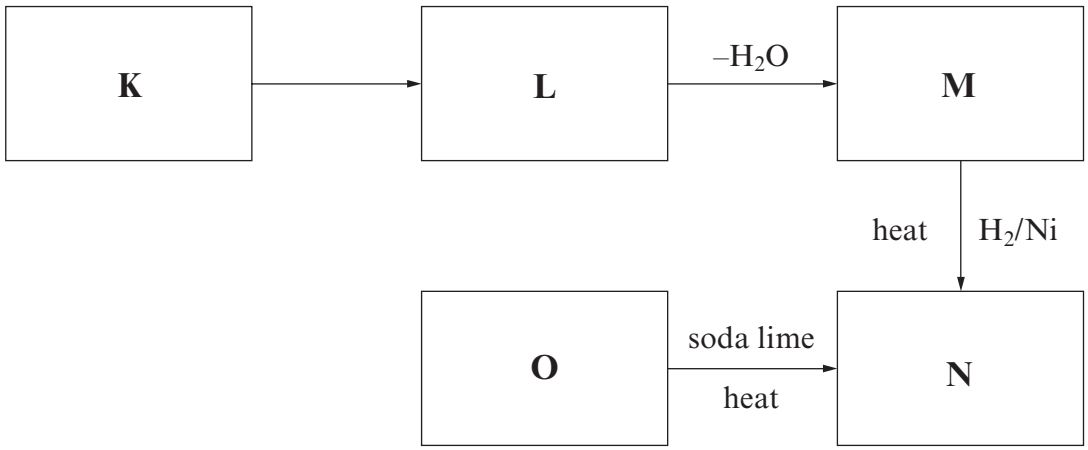
Total [15]

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.

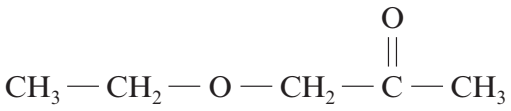
(i) Use **all** the information given to name compounds **X** and **Y**, giving your reasoning. Draw the displayed formula for isomer **T**. [4]

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.



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]

WJEC
CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET FOR USE WITH CH4

P.M. THURSDAY, 26 January 2012

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

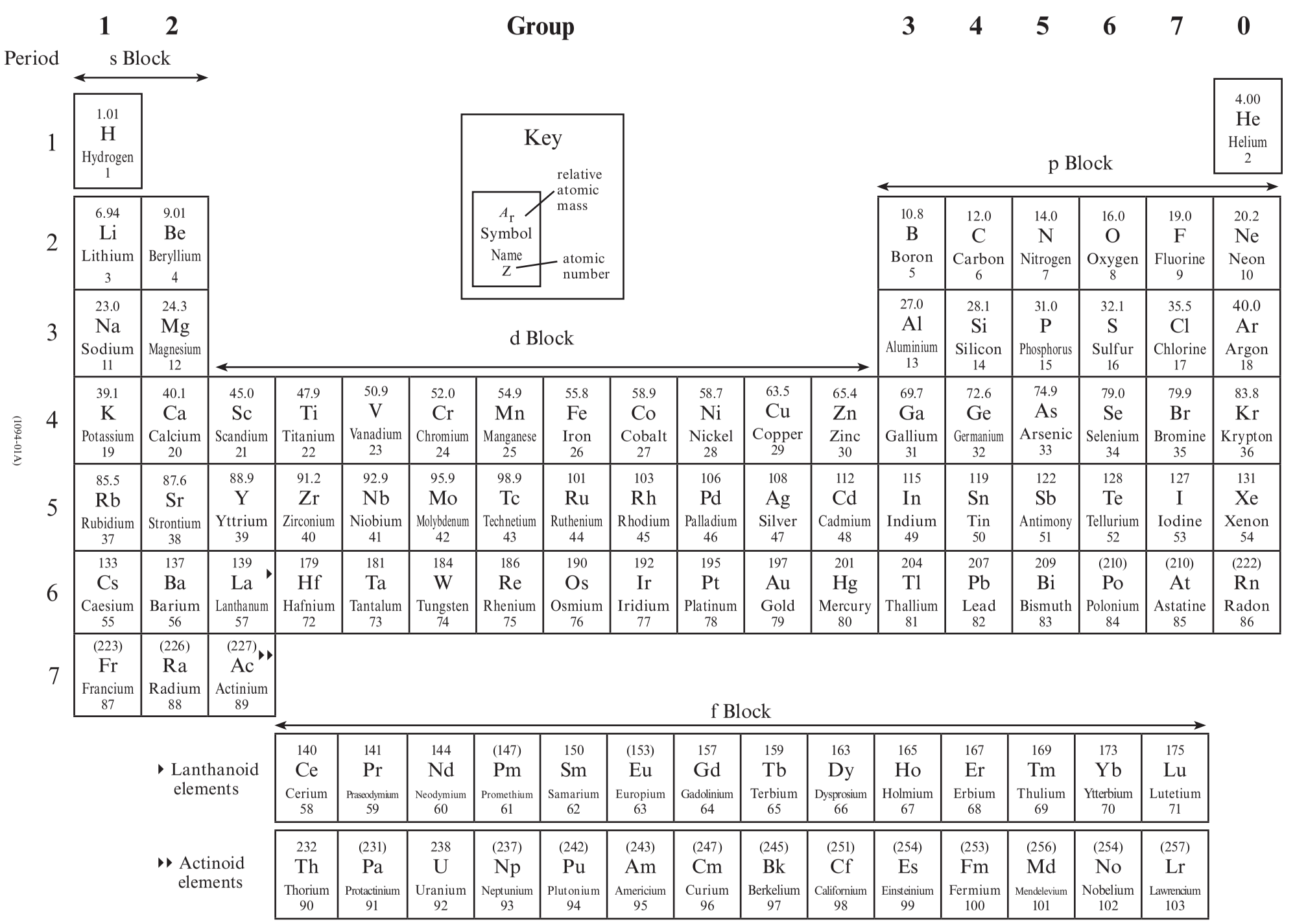
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift /ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_2-C(=O)-$	2.5 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
R—OH	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

JANUARY 2012

(b) (i) It contains an unpaired electron [1]

(ii) I $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ [1]

II A radical reacts to produce a new radical (that can continue the process) [1]

(iii) C_7H_{16} [1]

(iv) (Bond fission where a covalent bond breaks) and each atom receives an electron [1]

Total [13]

Q.9 (a) Hydrogen bonding occurs between (1) oxygen, nitrogen or fluorine (1) of one molecule and hydrogen, which is bonded to oxygen / nitrogen / fluorine of another molecule (1)
Alkanes do not contain an O-H, N-H or F-H bond and cannot therefore hydrogen bond to water molecules (1) [4]

QWC *Candidates should have use 'a selection and form of writing appropriate to purpose and to complexity of subject matter'* [1]

(b) (i) The (purified) petroleum is separated by heating (1) due to the different boiling temperatures of different fractions (1)

OR the mixture is vaporised (1) and then condensed according to boiling temperatures (1) (as at the oil refinery) [2]

(ii) $CuCl_2$ Cu +2 CuCl Cu +1 (1)

(reduction occurs when) the oxidation number becomes less positive (1) [2]

(c) (i) Same molecular formula but a different structural formula / structure [1]

(ii) Both of the carbon atoms of the double bond have different atoms / groups bonded to them (1)
There is no free rotation about the double bond (1) [2]

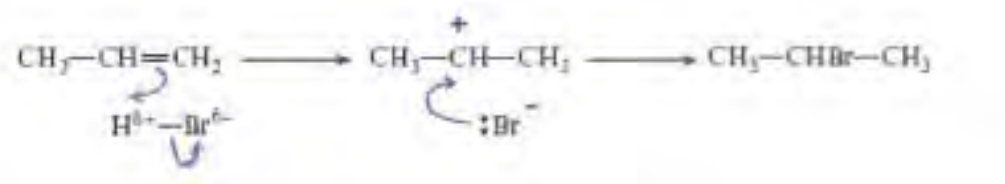
(iii) M_r of compound **A** is 146.3 / 146 (1)

Cost per mole is $\frac{146.3 \times 48 \times 100}{100 \times 73}$ = £96.20 (1)

(Accept £96.00 per mole if M_r of 146 has been used) [2]

Total [14]

Q.10 (a) (i)



curly arrows (1)
charges (1) [2]

(ii) Nucleophile hydroxide ion / OH^- / water (1)

Substitution the replacement of one functional group by another (1) [2]

(iii)

$CH_3CH_2Br + NaOH \rightarrow CH_2\ CH_2 + \mathbf{NaBr} + \mathbf{H_2O}$

(accept $\mathbf{Na^+}$ and $\mathbf{Br^-}$ in place of NaBr) [1]

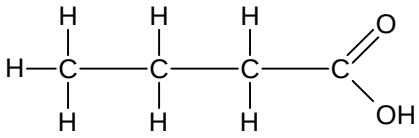
(b) M_r = 88 (1)

'M_r' R = 88 - (45) = 43 (1)

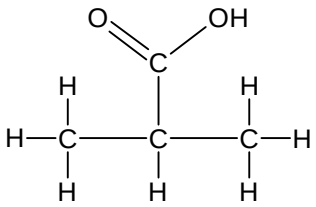
COOH

∴ R (an alkyl group) is C_3H_7

thus acid is



or



(1) [3]

(c) In graphite each carbon atom is bonded to three other carbon atoms (1) (using covalent bonding)
The other (outer) electron for each carbon atom is delocalised (1), throughout the structure and is able to move (1), conducting electricity
In iodine the two iodine atoms are bonded together (using covalent bonding) and there are no free electrons to carry the charge (1)
Mention of covalent bonding for either element (1) [5]

QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning (1)
Organisation of information clearly and coherently; use of specialist vocabulary where appropriate (1) [2]

Total [15]

SECTION B TOTAL [70]

GCE Chemistry – CH4

SECTION A

Q.1 (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]

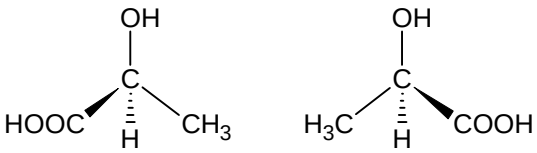
III Azo dye / azo compound [1]

Total [13]

Q.2

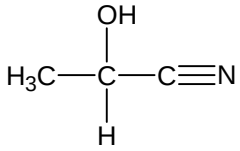
(a) (i) A compound that can rotate the plane of polarised light. [1]

(ii)



[1]

(iii)



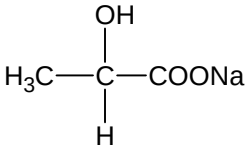
[1]

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

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

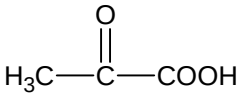
The rotating effect of one form exactly cancels out the effect of the other (1) [2]

(b) (i)



[1]

(ii)



[1]

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

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

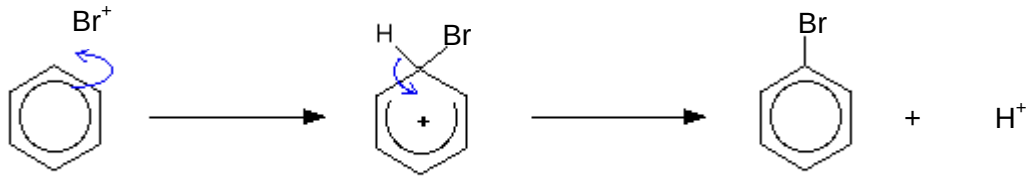
(iii) It exists as a zwitterion (1)

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

Total [12]

Q.3 (a) (i) Electrophilic substitution [1]

(ii) $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$



Formation of Br^+ (1), curly arrows (1), intermediate (1) [3]

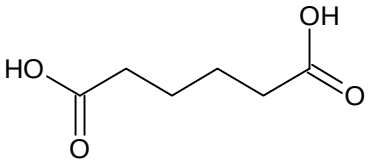
(b) (i) The extra stability in the benzene molecule due to electron delocalisation / the difference in energy between the experimental ΔH^θ reaction for benzene and the ΔH^θ reaction according to the Kekulé structure [1]

(ii) If benzene had 3 double bonds enthalpy change would be 3 x –120 = –360 kJ mol^{-1} (1)

Delocalisation energy is difference between –360 and –208 = 152 kJ mol^{-1} (1) [2]

(c) Benzene is carcinogenic / toxic [1]

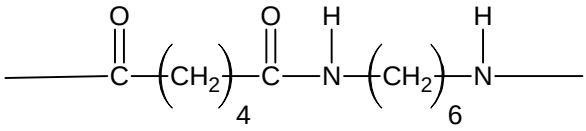
(d) (i) [1]



(ii) Reduction [1]

(iii) 1, 6-diaminohexane [1]

(iv) [1]



(v) Polyamide [1]

(vi) 226 tonnes nylon require 156 tonnes benzene (1)

800 tonnes nylon require 800 x $\frac{156}{226}$ = 552 tonnes (1) [2]

Total [15]

SECTION A TOTAL [40]

SECTION B

Q.4 (a) (i) Moles NaOH = 5.675×10^{-3} (1)

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

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

Contains CH_3CO due to positive iodoform test (1)

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

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

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

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

M is C_3H_6 (1)

N is C_3H_8 (1) [3]

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

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

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

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

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

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

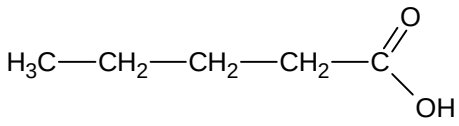
Moles = 3.074/150.1 = 0.0205 (1) [2]

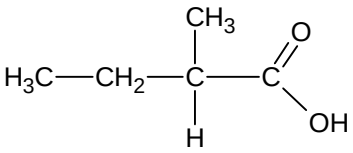
(v) Maximum mass = 0.0205 x 122 = 2.50 g (1)

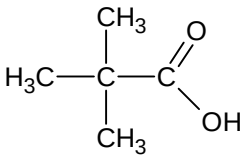
% yield = 1.45/2.50 = 58.0% (1) [2]

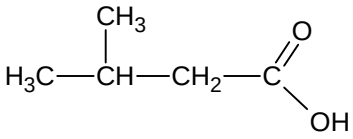
(vi) Hydrolysis not complete / equilibrium forms / C_6H_5COOH slightly soluble in water / two stages so some loss at both / mass lost during recrystallisation [1]

Total [20]

Q.5 (a) **P** is  (1)

Q is  (1)

R is  (1)

S is  (1)

[4]

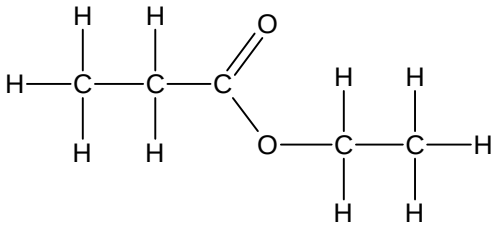
(b) (i) **T** neutral and sweet-smelling therefore an ester (1)

Infrared spectrum at 1750 cm^{-1} shows C=O and at 3000 cm^{-1} shows O–H therefore **X** is an acid (1)

Y is an alcohol, formed from ethanal must be ethanol (1)

5 carbons in ester therefore **X** must be propanoic acid (1)

Structure of **T** is

 (1)

(Maximum 4 marks) [4]

QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning (1)

Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1) [2]

(ii) I Reagent to form **Y** is $NaBH_4$ / $LiAlH_4$ [1]

II Sulfuric acid acts as a catalyst / removes water so pushes equilibrium to right [1]

(c) $CH_3(CH_2)$ 0.1 to 2.0 ppm triplet (1)

$(CH_3)CH_2O$ 3.5 to 4.0 ppm quadruplet (1)

CH_2CO 2.5 to 3.0 ppm singlet (1)

CH_3CO 2.0 to 2.5 ppm singlet (1) [4]

(d) Isomer **P** (1)

Only **P** can form hydrogen bonds between molecules (1)

Hydrogen bonds are the strongest intermolecular bonds / need more energy to break hydrogen bonds (1) [3]

QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate [1]

Total [20]

SECTION B TOTAL [40]

Surname	Centre Number	Candidate Number
Other Names		2

WJEC CBAC

GCE A level

1094/01

CHEMISTRY – CH4

P.M. MONDAY, 14 January 2013

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.
  Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

Examiner only

SECTION A

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

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

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

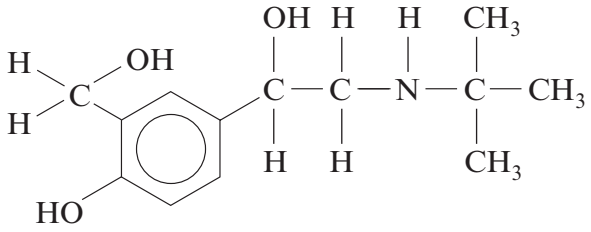
(ii) A neutral sweet-smelling compound [1]

(iii) An α-amino acid [1]

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

Examiner only

(b) The active compound in Ventolin® inhalers used by asthma sufferers is salbutamol, which shows optical isomerism.



salbutamol

(i) Indicate a chiral centre in this molecule by labelling it with an asterisk (*). [1]

(ii) State how the optical isomers of salbutamol could be distinguished from each other. [1]

.....

.....

(iii) Suggest a reason why only one optical isomer of salbutamol is used as a pharmaceutical. [1]

.....

(iv) Draw the displayed formula of the likely organic product formed when salbutamol is refluxed with acidified $K_2Cr_2O_7$. [2]

Examiner only

(c) (i) Arrange the following molecules in order of **increasing** acidity. [1]

ethanoic acid *ethanol* *ethylamine* *phenol*

least acidic ..... most acidic

(ii) Explain the difference in acid-base properties of ethylamine and phenol. [4]

.....

.....

.....

.....

.....

Total [14]

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Examiner only

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

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

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

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

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

.....

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

.....

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

.....

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

.....

.....

(c) Propanone can react with hydrogen cyanide.

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

.....

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

Total [12]

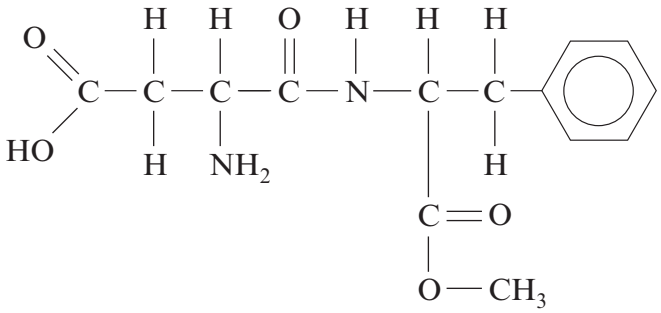
3. *Read the passage below and then answer the questions in the spaces provided.*

Tastes in food

The sensation of taste can be categorized into five basic tastes: sweet, bitter, sour, salty and umami. Humans receive tastes through sensory organs called taste buds concentrated on the top of the tongue. Pungency also helps us to describe the tastes that we encounter in food. Some of these tastes are described below.

Sweetness

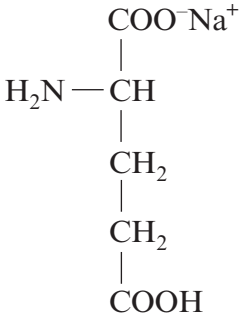
One theory in the 1960s proposed that to be sweet, a compound must contain a hydrogen bond donor (AH) and a hydrogen bond accepter (B).
Human taste buds are much more sensitive to synthetic sweeteners than to naturally-occurring sugars. For example, aspartame is 200 times sweeter than sucrose.



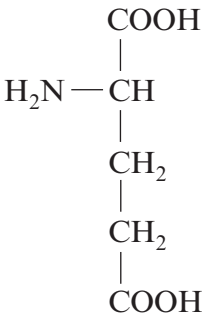
aspartame

Umami

Umami is a Japanese word meaning 'good flavour' or 'good taste' and is described as a savoury or meaty taste. Monosodium glutamate (MSG), the monosodium salt of glutamic acid, was developed as a food additive in 1908 by a Japanese scientist and produces a strong umami taste.



MSG



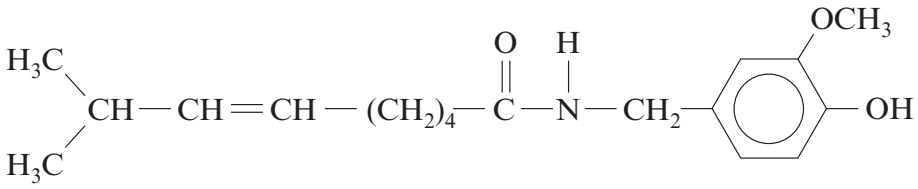
glutamic acid

Other foods that have always been popular as flavourings are now known to be rich in umami substances. These include seaweeds, fish, mushrooms and tomatoes.
Like other basic tastes, MSG improves pleasantness only in the right concentration. An excess of MSG quickly ruins the taste of a dish e.g. in clear soup the 'pleasantness score' rapidly falls with 1 g or more of MSG per 100 cm^3.

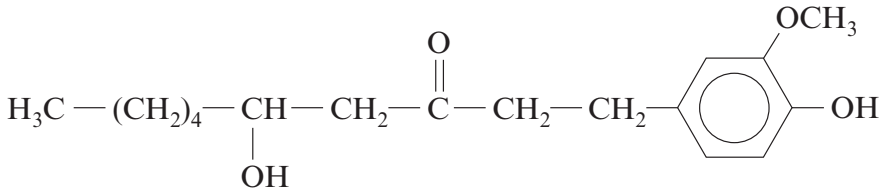
Examiner only

Pungency

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



capsaicin (chilli peppers)



gingerol (ginger)

– End of passage –

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

.....

.....

.....

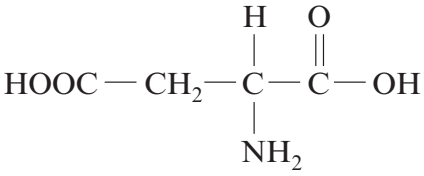
.....

.....

.....

Examiner only

(b) Aspartame *(line 10)* is a methyl ester of a dipeptide formed from two α-amino acids. The structure of one of the acids is as shown below.



Draw the structure of the other α-amino acid. [1]

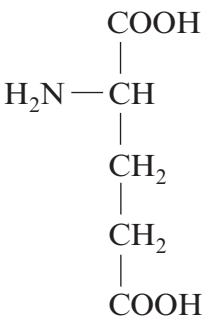
(c) Glutamic acid *(line 16)* is amphoteric. Explain the meaning of the term *amphoteric* and why glutamic acid exhibits amphoteric behaviour. [2]

.....

.....

.....

(d) Draw the **skeletal** formula of glutamic acid. [1]



glutamic acid

Examiner only

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

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

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

Reagent(s) .....

Observation .....

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

Reagent(s) .....

Observation .....

Total [14]

Total Section A [40]

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.

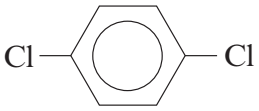
Your answer should include

- 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.

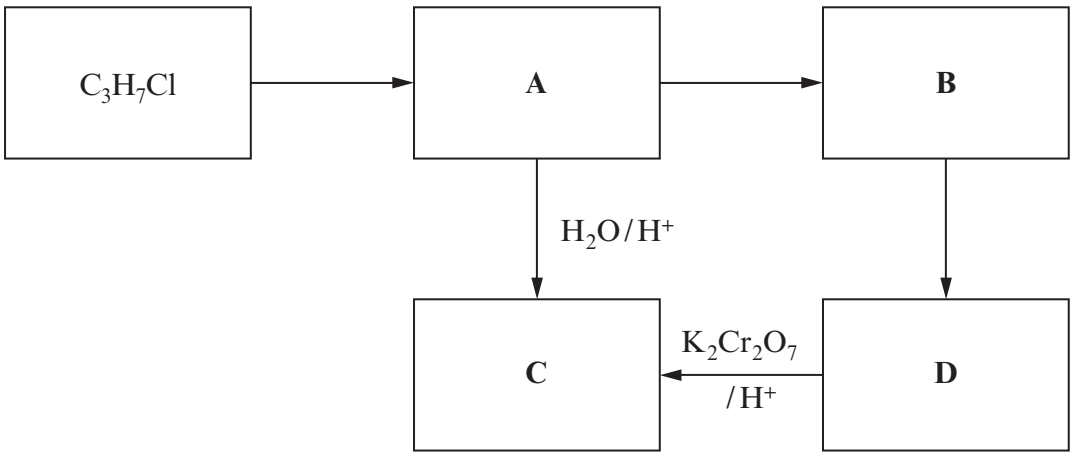
(i) State why the temperature is kept under 10 °C. [1]

(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.

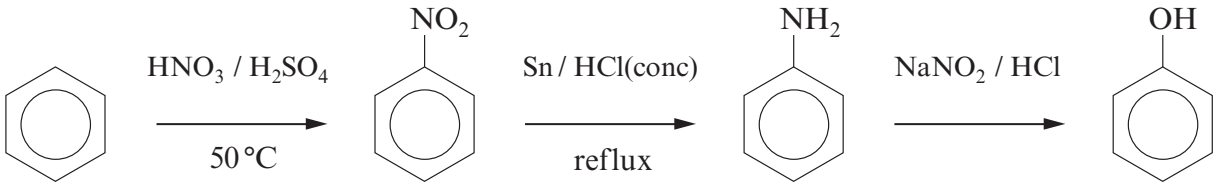
(i) Calculate the relative molecular mass of compound **B**. Show your working. [2]

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

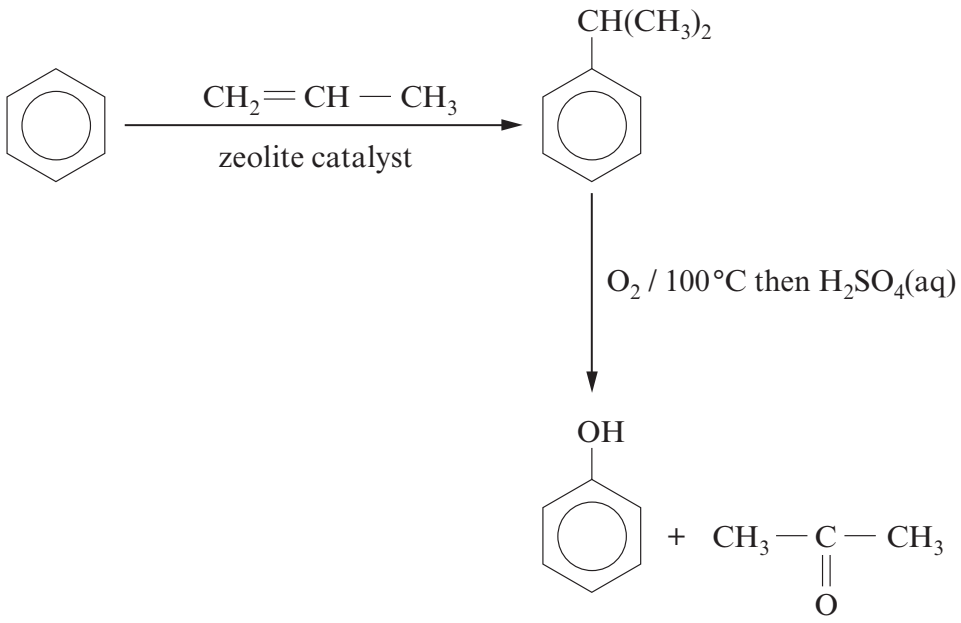
(b) C_3H_7Cl exists as two isomers. Sketch the **low** resolution NMR spectra of both isomers giving the approximate chemical shift (ppm) and the relative area of each peak. [4]

QUESTION 5 CONTINUES ON PAGES 14 AND 15

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



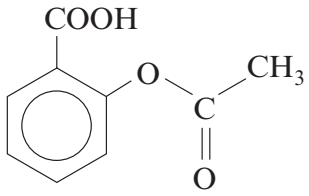
However, the industrial method of making phenol uses a different route as shown below.



(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]

(d) Phenol can be converted into aspirin.



aspirin

When 58.75 g of phenol was reacted with the appropriate chemicals, the yield of aspirin was 65%. Calculate the mass of aspirin produced in this process. [3]

Total [20]

Section B Total [40]

END OF PAPER

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET FOR USE WITH CH4

P.M. MONDAY, 14 January 2013

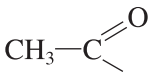
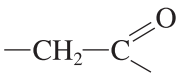
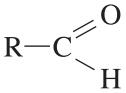
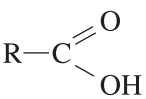
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

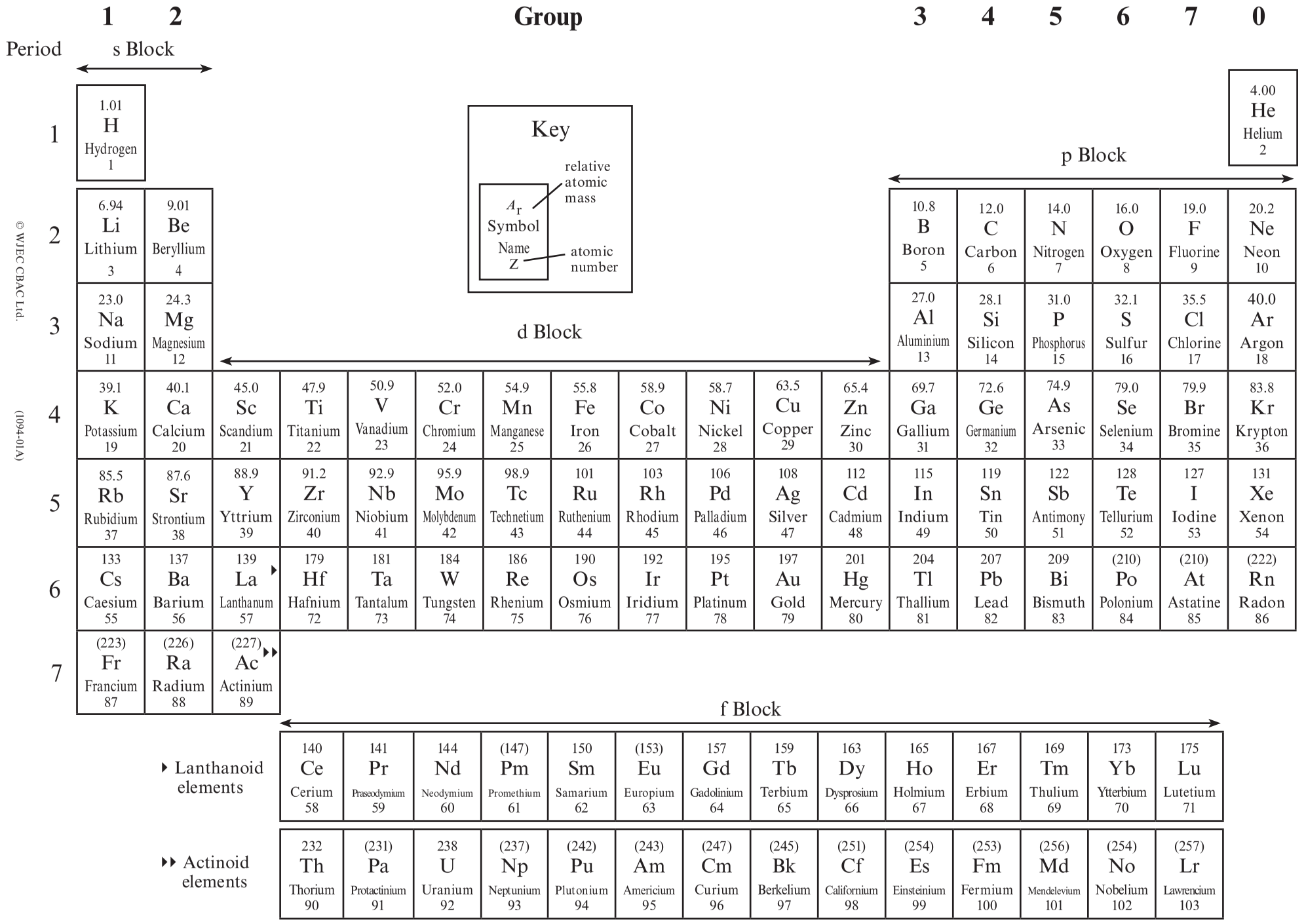
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
$R-CH_2Cl$, $R-CHCl-R$	3.0 to 4.3
R—OH	4.5 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

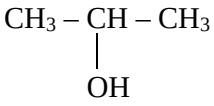
CHEMISTRY
AS/Advanced

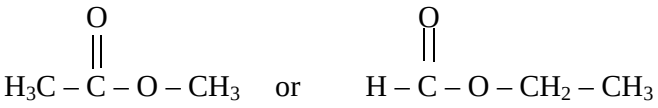
JANUARY 2013

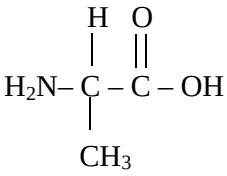
GCE CHEMISTRY - CH4

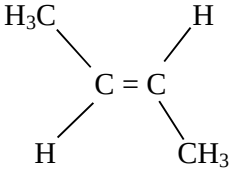
JANUARY 2013 MARK SCHEME

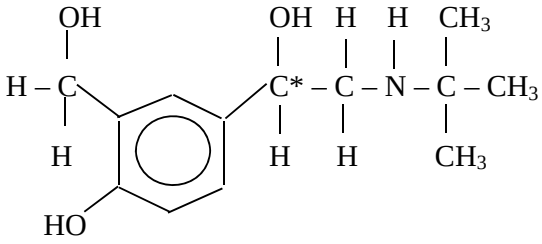
Section A

1. (a)(i)  [1]

(ii)  [1]

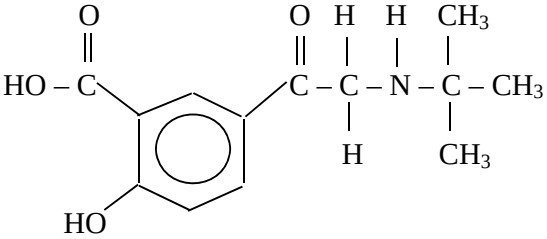
(iii)  [1]

(iv)  (or Z form) [1]

(b)(i)  [1]

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

(iii) Side effects from other optical isomer / lower dose needed / improved pharmacological activity / only one isomer has correct orientation to bind with biological molecule [1]

(iv)  [2]

(1 mark for acid (accept aldehyde), 1 mark for ketone)

(c)(i) Ethylamine, ethanol, phenol, ethanoic acid [1]

(ii) Ethylamine is basic because it accepts a proton readily (1) due to the lone pair of electrons on the nitrogen. (1)
Phenol is acidic because it loses a proton / the anion formed is stabilised (1)
by delocalisation of the negative charge over the benzene ring. (1)
(Accept description e.g. in phenoxide ion lone pairs of electrons on oxygen become delocalised with electrons in benzene ring.) [4]

Total [14]

2. (a)

	Butan-2-ol	Ethanal	Ethanol	Propanone
2,4-DNP	No reaction	Yellow-orange precipitate	No reaction	Yellow-orange precipitate
Tollens' reagent	No reaction	Silver mirror	No reaction	No reaction
I_2/NaOH	Yellow precipitate	Yellow precipitate	Yellow precipitate	Yellow precipitate

(1 mark for each column) [4]

(b)(i) Electrophilic addition [1]

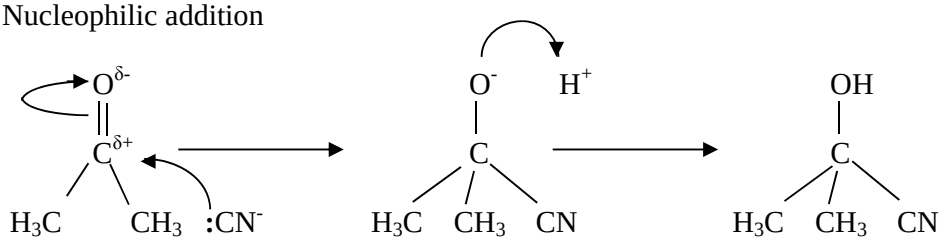
(ii) Carbonium ion / carbocation / electrophile [1]

(iii) Bromination / HBr addition / hydrogenation[1]

(iv) Secondary carbocation more stable than primary carbocation [1]

(c)(i) Nucleophilic addition [1]

(ii)



[3]

1 mark electron movement
1 mark charges

1 mark intermediate
and electron movement

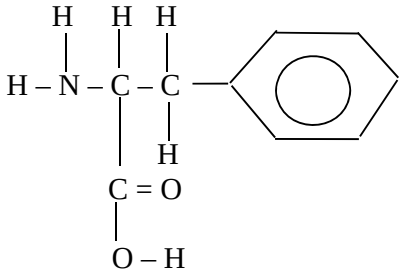
(Accept $CN^{\delta-} - H^{\delta+}$ for CN^-)

Total [12]

3. (a) Intermolecular bond formed (1) when hydrogen attached to a highly electronegative atom (1) is bonded to an electronegative atom attached to hydrogen (in another molecule) (1) forming a very strong dipole – dipole attraction (1) [3]
(maximum 3 marks)

QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning [1]

(b)

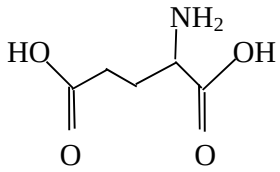


[1]

(c) Behaves as / can react with an acid or a base (1)

-COOH is an acidic group / donates proton, $-NH_2$ is a basic group / accepts proton (1) [2]

(d)



[1]

(e) Moles MSG = 1/169.08 = 5.91×10^{-3} (1)

Concentration = $5.91 \times 10^{-3} / 0.1 = 5.91 \times 10^{-2}$ (1) [2]

(f) (Neutral) $FeCl_3$ / Br_2 (1)
Purple colour / white precipitate (1) [2]

(g) 2,4-Dinitrophenylhydrazine / acidified sodium dichromate (1)

Yellow-orange precipitate / orange to green colour change (1) [2]

Total [14]

Total Section A [40]

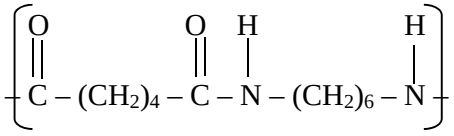
Section B

4. (a) For synthetic polymer:

Monomers: 1,6-Diaminohexane / ethane-1, 2-diol (1)

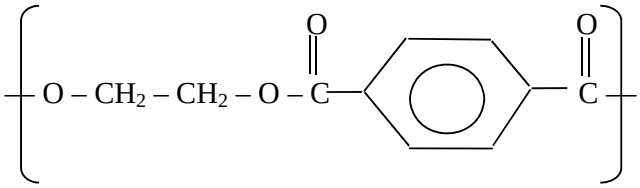
Hexanedioic acid / benzene-1,4-dioic acid (1)

Structure:



(1)

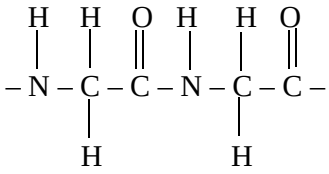
or



For natural polymer:

Monomers: aminoethanoic acid / 2-aminopropanoic acid (1)

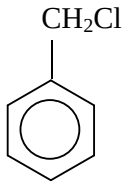
Structure: e.g.



(1)

[5]

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

(b) (i) 

[1]

(ii) 1,4-dichlorobenzene [1]

(iii) Chlorine (in the absence of ultraviolet light) (1)

$AlCl_3$ / $FeCl_3$ (as a halogen carrier) (1) [2]

(iv) Heat with NaOH (aq) (1)

add HNO_3(aq) followed by $AgNO_3$(aq) (1)

F gives white precipitate, **G** does not (1)

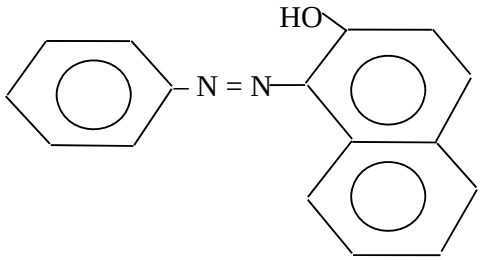
In **F**, the C–Cl bond is polarised / contains $C^{\delta+}$ or undergoes nucleophilic substitution (1)

In **G** due to delocalisation of the π electron cloud of the ring with the p-orbital electrons of the chlorine (1)

the C–Cl bond is too strong to break/ does not undergo nucleophilic substitution (1) [6]

QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate [1]

(c)(i) To prevent decomposition of benzenediazonium chloride / HNO_2 [1]

(ii) 

[1]

(iii) A chromophore is the group of atoms responsible for the colour of the compound (by causing absorption in the visible region of the spectrum) [1]

Total [20]

5. (a)(i) Moles HCl = 5.4×10^{-3} (1)

M_r **B** = $\frac{0.395}{0.0054}$ = 73.1 (1) [2]

(ii) **B** is basic therefore must be amine (1)

C reacts with Na_2CO_3 therefore must be an acid (1)

D is oxidised to **C** therefore must be an alcohol (1)

A hydrolyses to acid but does not contain oxygen therefore must be nitrile (1)

B is $CH_3CH_2CH_2CH_2NH_2$ (1)

C is $CH_3CH_2CH_2COOH$ (1)

D is $CH_3CH_2CH_2CH_2OH$ (1)

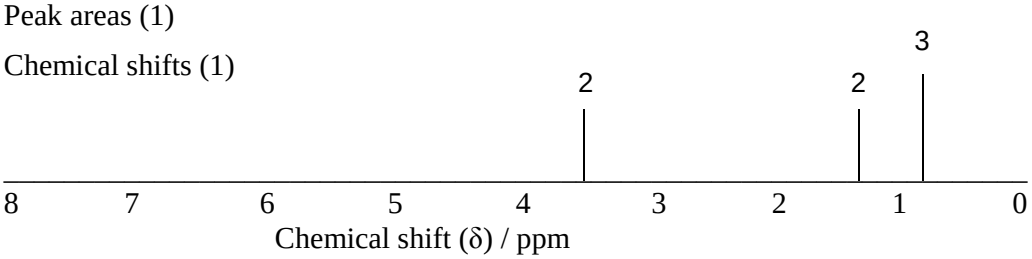
A is $CH_3CH_2CH_2CN$ (1) [8]

(4 marks structures – if 3 carbons in chains penalise only once
4 marks reasons – accept alternative reasons)

(b) $CH_3CH_2CH_2Cl$

Peak areas (1)

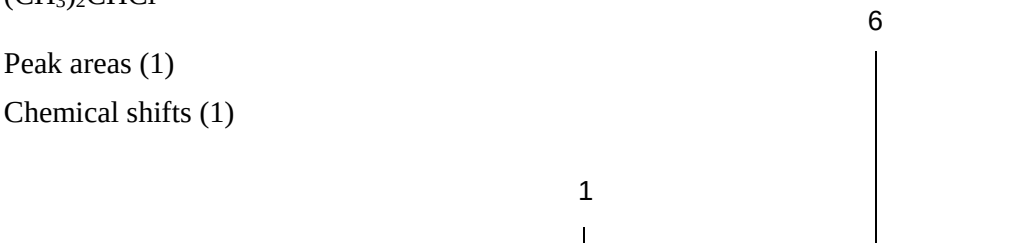
Chemical shifts (1)



$(CH_3)_2CHCl$

Peak areas (1)

Chemical shifts (1)



[4]

(c)(i) 2 steps instead of 3 / CH_3COCH_3 can be sold / reagents are cheaper / gives a higher yield / easier to extract phenol / phenol formed more quickly / fewer reactants [2]
(Accept any 2)

(ii) Lower temperature required / catalyst costs less / catalyst less likely to break up / catalyst less toxic or safer [1]

(d) Moles phenol = 58.75/94.06 = 0.625 (1)

Maximum mass aspirin = 0.625 × 180.08 = 112.55 g (1)

65% yield, therefore mass aspirin = 73.16 g (1) [3]

Total [20]

Total Section B [40]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY – CH4

P.M. MONDAY, 13 January 2014

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**13**	
	2.	**13**	
	3.	**14**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1094 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

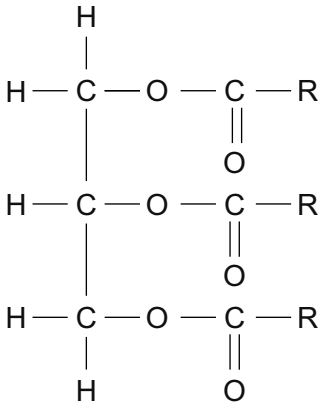
Examiner only

SECTION A

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

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

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



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

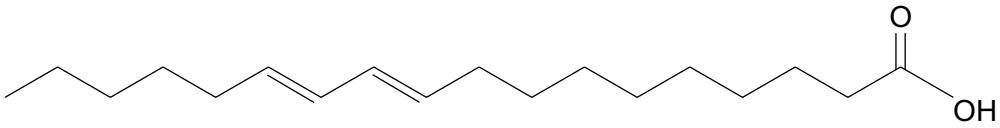
Reagent(s) .....

Condition(s) .....

Equation

Examiner only

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



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

Reagent(s) .....

Observation(s) .....

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

.....

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

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

Maximum mass = ... g

QUESTION CONTINUES ON PAGE 4

Examiner only

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

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

Empirical formula .....

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

.....

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

.....

.....

Total [13]

13

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Examiner only

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]

.....

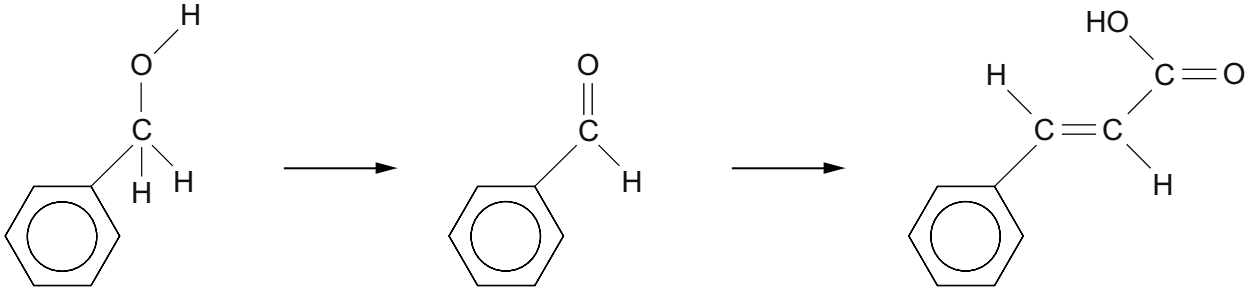
.....

.....

.....

Examiner only

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



phenylmethanol benzenecarbaldehyde cinnamic acid

(i) Give the reagent(s) and condition(s) required to obtain a sample of benzenecarbaldehyde from phenylmethanol. [2]

Reagent(s) .....

Condition(s) .....

(ii) The conversion of phenylmethanol to benzenecarbaldehyde has a yield of 86 %. Calculate the mass of benzenecarbaldehyde that could be produced from 10.0 g of phenylmethanol. [3]

1094 010007

Mass = ... g

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

.....

.....

.....

.....

.....

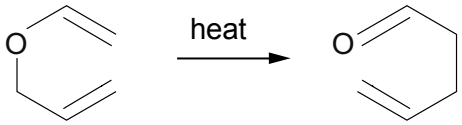
Total [13]

13

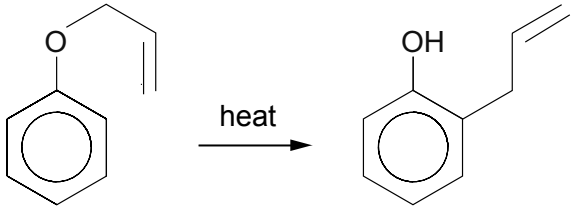
3. *Read the passage below and then answer the questions in the spaces provided.*

Rearrangement reactions

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



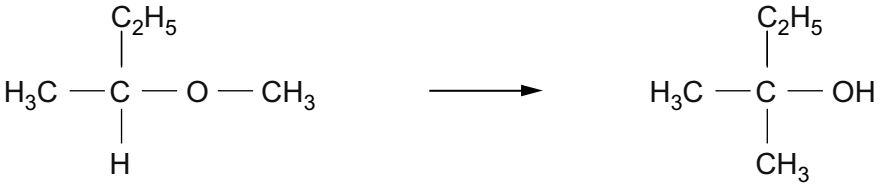
Claisen rearrangement



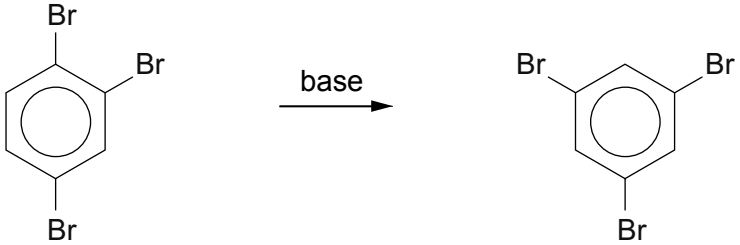
aromatic Claisen rearrangement

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

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



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



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

– End of passage –

Examiner only

(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]

.....

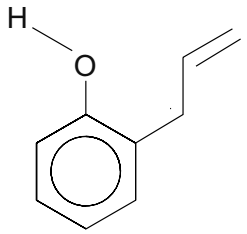
.....

(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]

.....

.....

.....

.....

.....

.....

Examiner only

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

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

Classification of mechanism .....

Total [14]

Total Section A [40]

14

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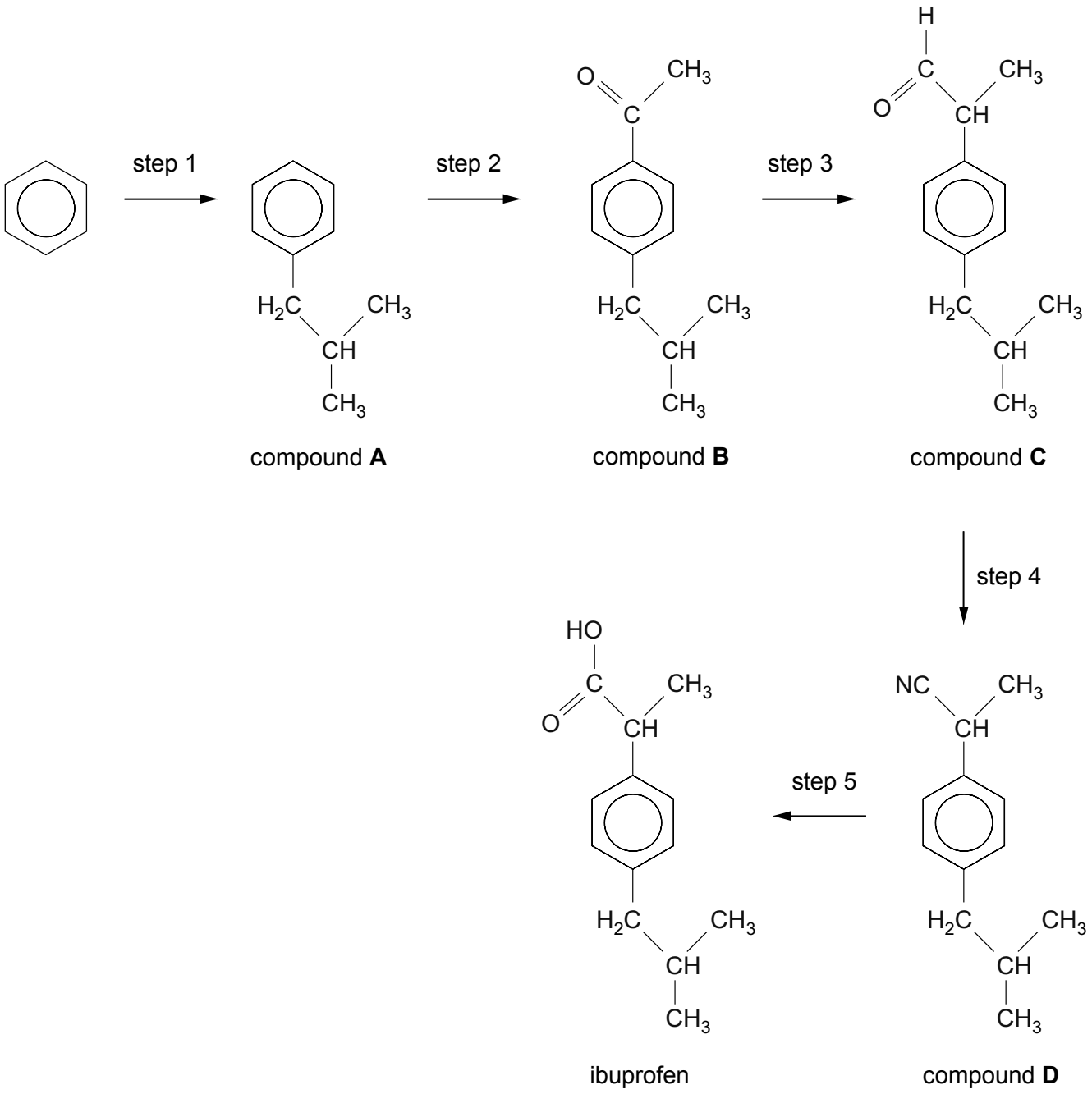
SECTION B

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]

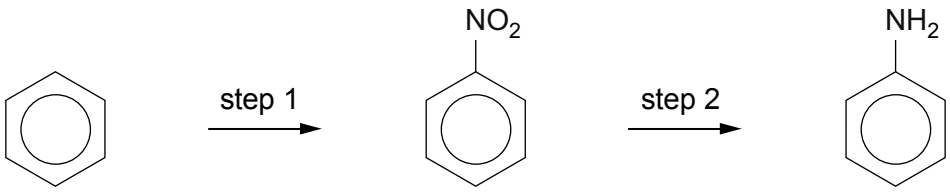
5. This question focuses on molecules that contain the $-NH_2$ group.

(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]

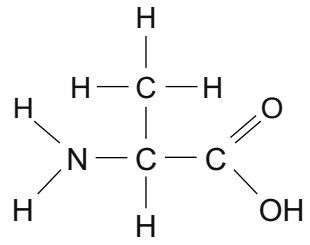
III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]

(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

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. MONDAY, 13 January 2014

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
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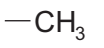
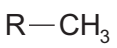
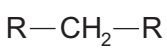
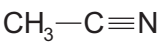
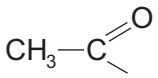
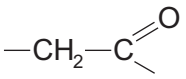
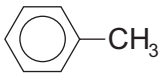
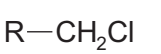
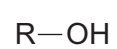
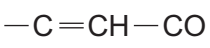
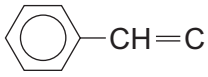
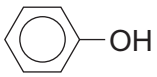
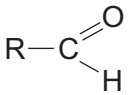
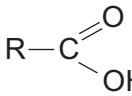
Nuclear Magnetic Resonance Spectroscopy

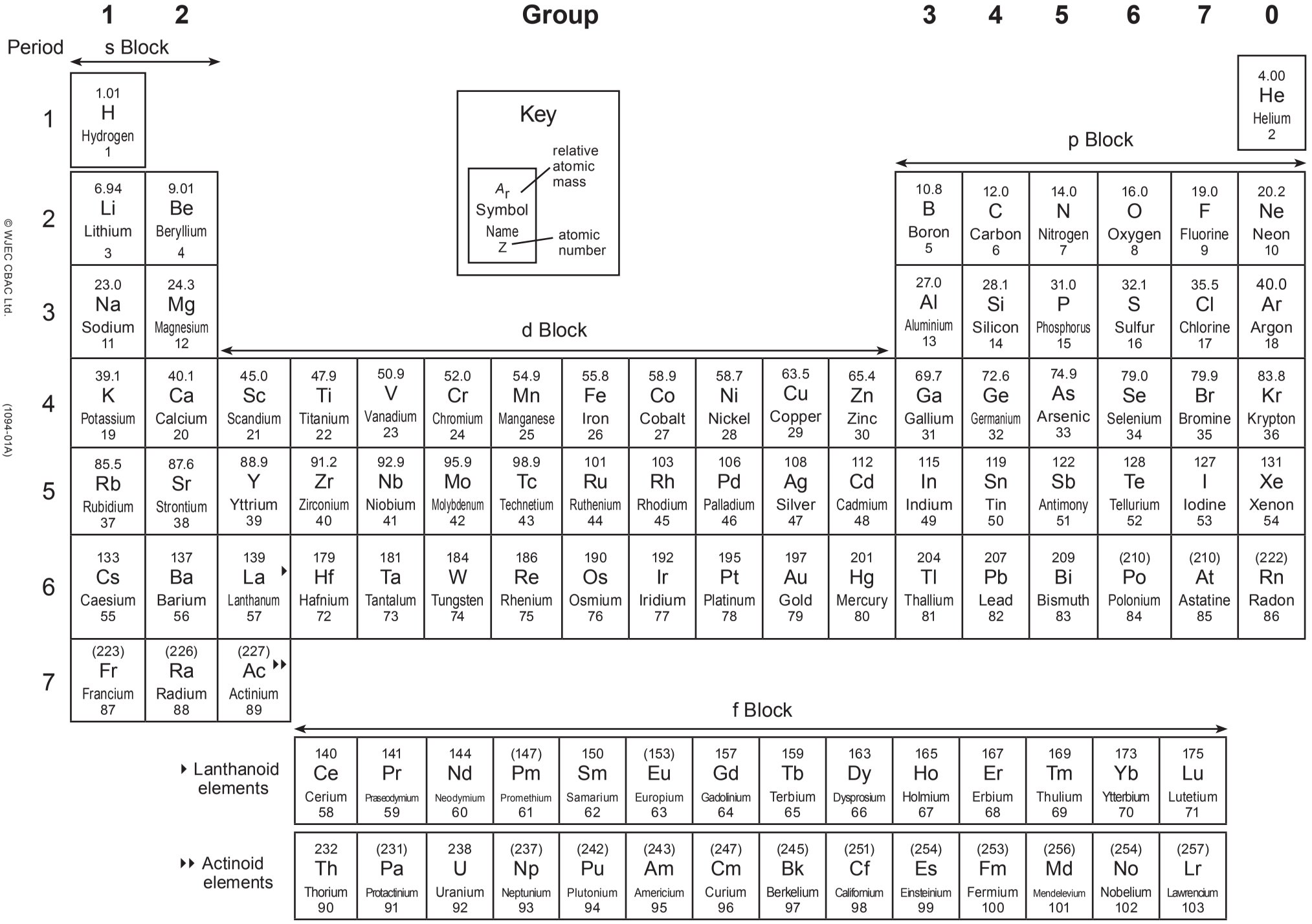
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
	0.1 to 2.0
	0.9
	1.3
	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
	3.3 to 4.3
	4.5 *
	5.8 to 6.5
	6.5 to 7.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE A level

1094/01-A

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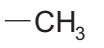
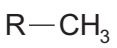
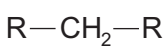
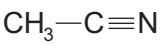
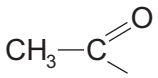
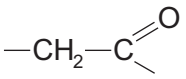
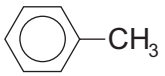
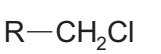
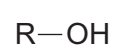
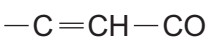
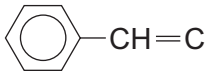
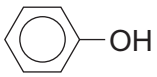
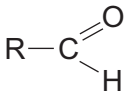
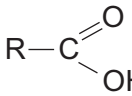
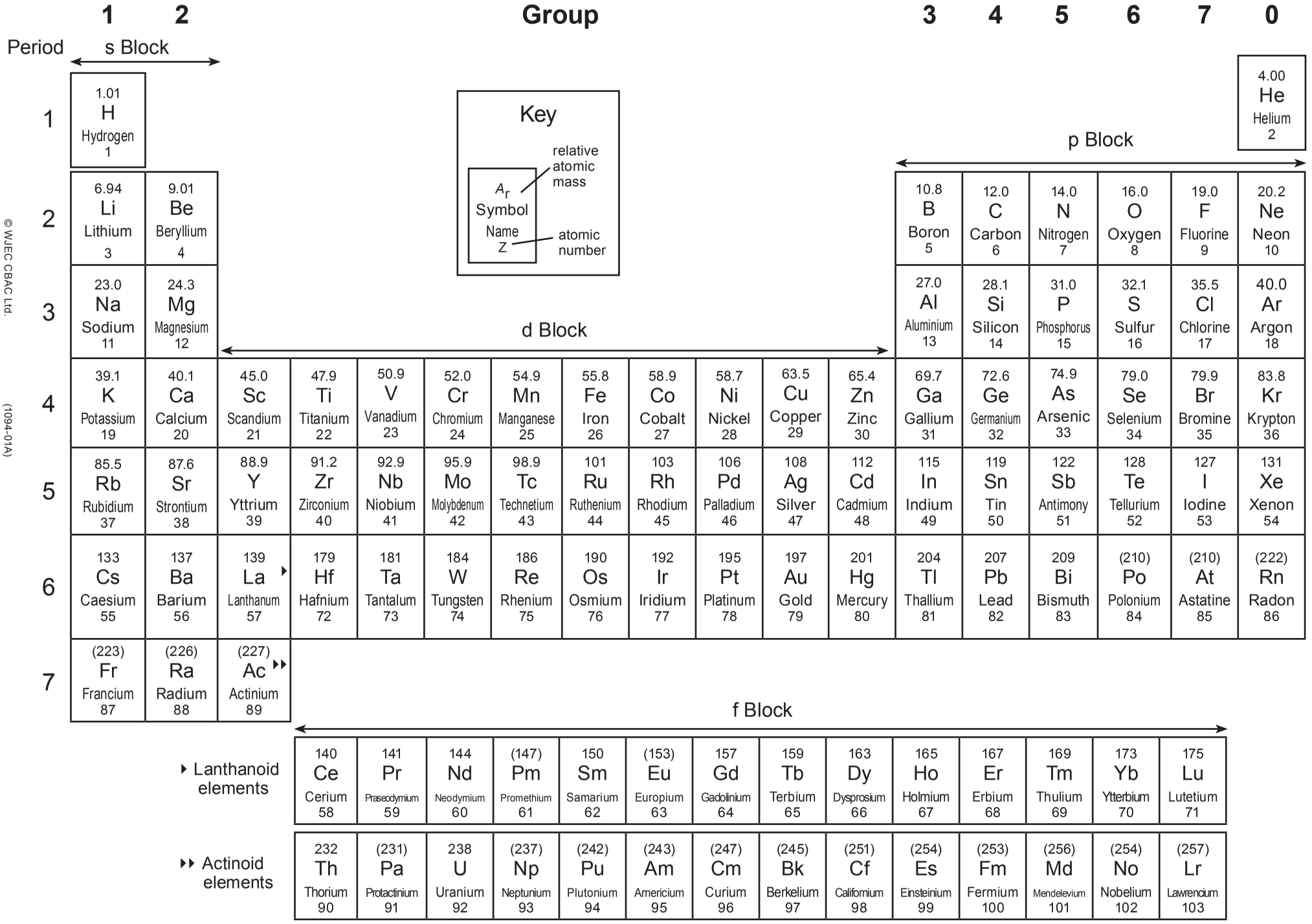
	0.1 to 2.0
	0.9
	1.3
	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
	3.3 to 4.3
	4.5 *
	5.8 to 6.5
	6.5 to 7.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

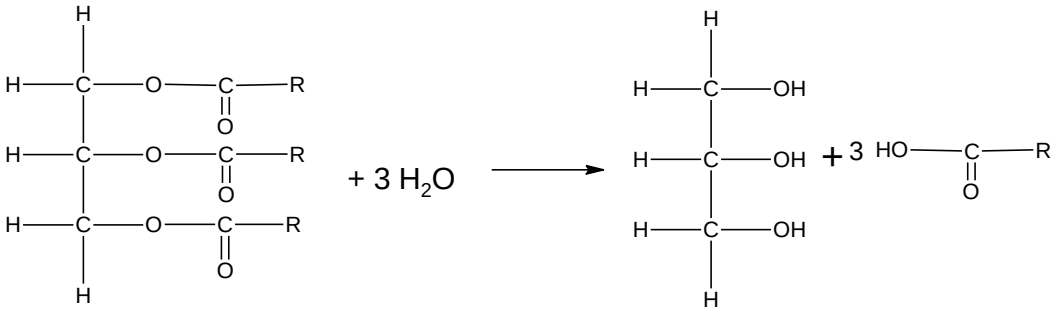
JANUARY 2014

CH4

Section A

Q.1 (a) Reagent(s): (aqueous) sodium hydroxide followed by acid (1)

Condition(s): Heat (to reflux) (1)



[IF NO ACID LISTED IN REAGENT, THEN EQUATION SHOULD CONTAIN SODIUM SALTS] (1) [3]

(b) (i) Reagent(s): (aqueous) bromine (1)
Observation(s): Changes from orange to colourless (1) [2]

(ii) Nickel / Platinum / Palladium [1]

(iii) Moles of hydrogen gas = $1.15 \div 24.0 = 4.79 \times 10^{-2}$ mol (1)
Moles of stearic acid produced = $4.79 \times 10^{-2} \div 2 = 2.40 \times 10^{-2}$ mol (1)
Mass of stearic acid = $2.40 \times 10^{-2} \times 284 = 6.80$ g (1) [3]

(c) (i) **C** $69.7 \div 12 = 5.808$ **H** $11.7 \div 1.01 = 11.584$ **O** $18.6 \div 16 = 1.163$ (1)
Empirical formula = $C_5H_{10}O$ (1) [2]

(ii) $C_{10}H_{20}O_2$ [1]

(d) e.g. biodiesel is renewable/won't run out / carbon neutral
do not accept 'produces less carbon dioxide' [1]

Total [13]

Q.2 (a) Chromophore [1]

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

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

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

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

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

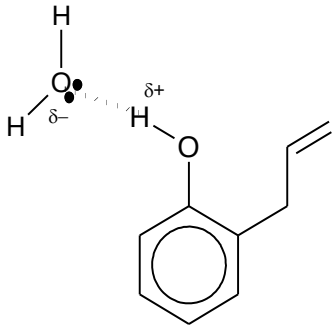
Total [13]

Q.3 (a) Isomers [1]

(b) (i) Peak at 2500-3550 cm^{-1} present in product but not reactant [1]

(ii) Add $FeCl_3$ (1)
Forms a purple solution (1) do not accept 'precipitate' [2]

(iii) 1 mark for correct location of hydrogen bond; 1 mark for dipole OR lone pair
e.g.



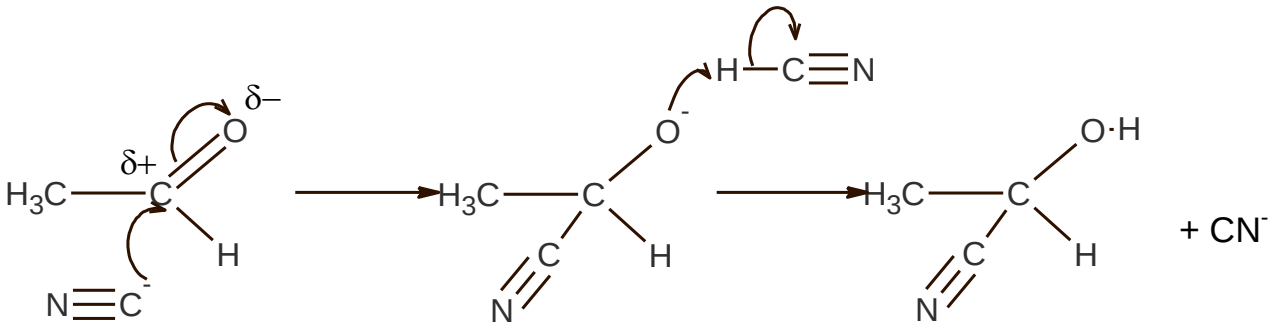
[2]

(c) Aromatic Claisen product is more acidic / better proton donor than product of 1,2-Wittig rearrangement (1)

The 1,2-Wittig rearrangement product is an alcohol, so the charge on the **anion** formed is localised / the **anion** is unstable (1)
The product of the aromatic Claisen rearrangement is a phenol, so the charge on the anion can be delocalised which stabilises it (1)
(Must be reference to 'anions'; (1) mark awarded for 'stability of anions' if no reference to delocalisation) [3]

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

(d) 1 mark for arrows in first stage; 1 mark for correct intermediate; 1 mark for arrow giving gain of proton in second stage (from HCN or from H^+); 1 mark for bond polarity – max 3 marks; lose 1 if incorrect final structure



Mechanism: Nucleophilic addition (1) [4]

Total [14]

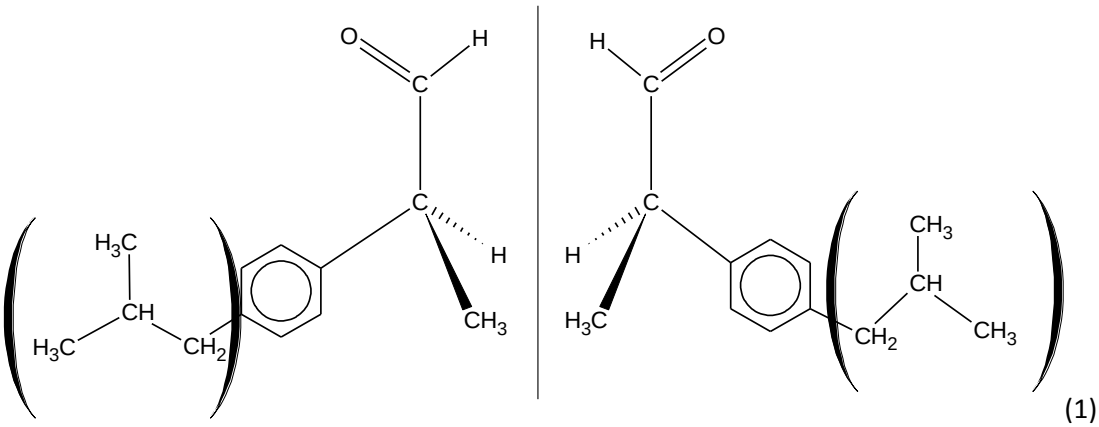
Total Section A [40]

Q.4 (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]

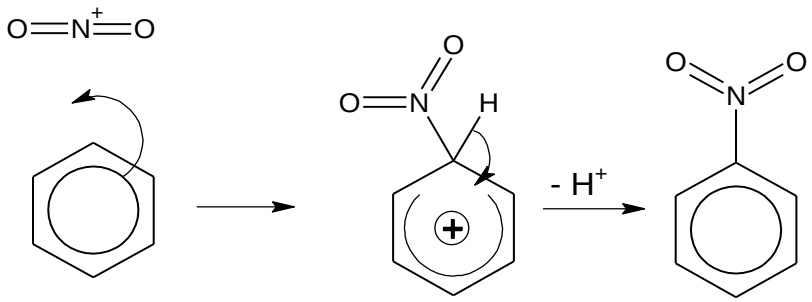
Total [20]

Q.5 (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)

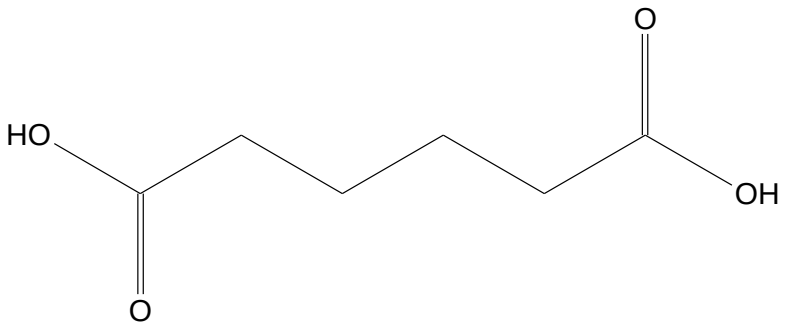


[3]

II (fractional) distillation / steam distillation [1]

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

(b) (i)



[1]

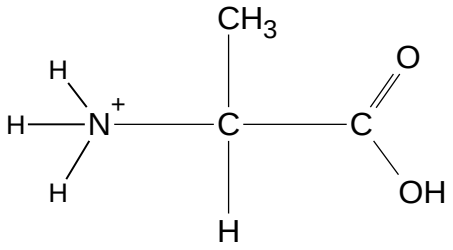
(ii) Addition polymerisation makes one product only /
Condensation produces one product plus a small molecule like water (1)

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)

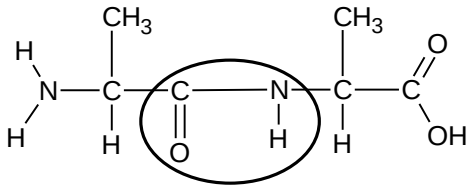
(max 2) [2]

(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]

Total Section B [40]

Candidate Name	Centre Number	Candidate Number
		2

GCE A level

1094/01

CHEMISTRY CH4

P.M. THURSDAY, 17 June 2010

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1094 01 01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

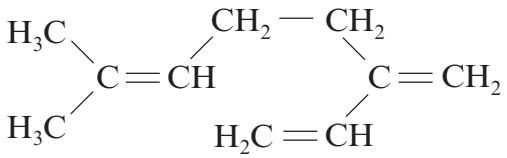
You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

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

1. *(a)* Terpenes are the primary constituents of the essential oils of many types of plants and flowers.
An example is myrcene, one of the most important chemicals used in the perfume industry because of its pleasant odour. It has the structure shown below.



(i) State the molecular formula of myrcene. [1]

.....

(ii) Draw the **skeletal** formula of myrcene. [1]

(iii) Myrcene reacts with hydrogen to form a saturated hydrocarbon in the same way as alkenes of general formula C_nH_{2n}.

I. Explain what is meant by the term *saturated* hydrocarbon. [1]

.....

.....

II. Using molecular formulae write an equation for this reaction. [1]

.....

(iv) Another terpene, α-farnasene, is responsible for the characteristic odour of green apples.
A 0.100 mol sample of α-farnasene reacted with 8.96 dm^3 of hydrogen to form a saturated hydrocarbon $C_{15}H_{32}$.
(1 mole of gas molecules occupy 22.4 dm^3 under these conditions.)

Calculate how many double bonds there are in each molecule of α-farnasene. [2]

.....

.....

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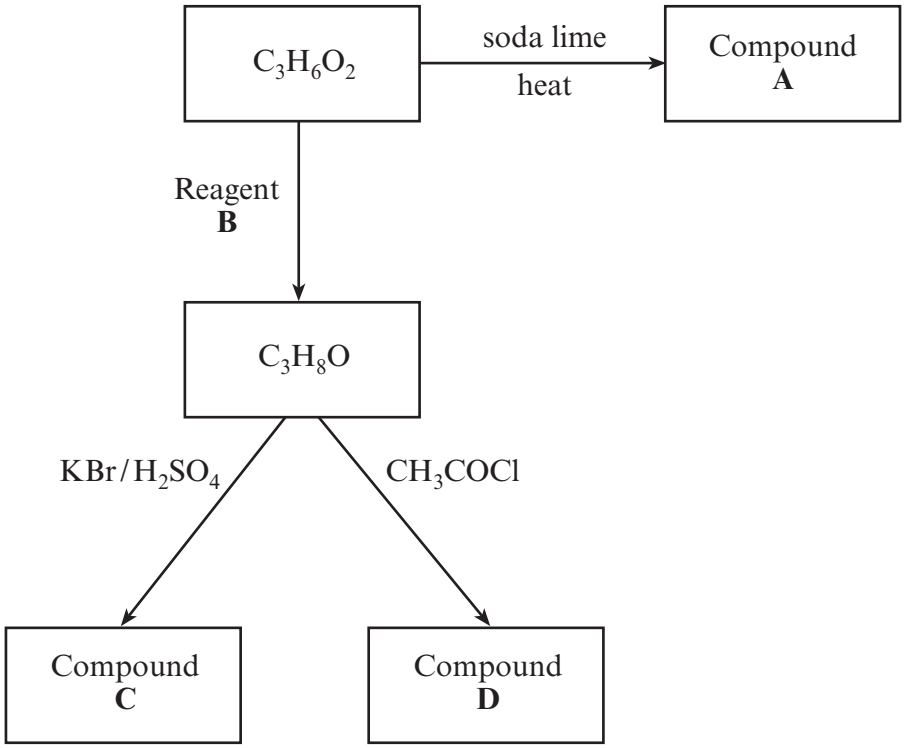
.....

Examiner only

(b) Study the reaction scheme shown below:



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

.....

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

.....

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

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

.....

Total [10]

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Examiner only

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

.....

.....

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

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

.....

.....

.....

.....

.....

.....

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

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

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

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

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

.....

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

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

.....

.....

.....

.....

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

.....

.....

.....

.....

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

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

.....

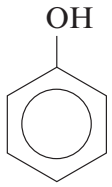
(ii) Draw, with the aid of curly arrows, the mechanism for this reaction. [3]

Total [15]

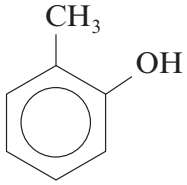
3. *Read the passage below and then answer the questions in the spaces provided.*

Phenol

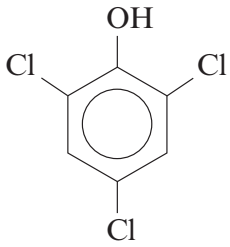
Phenol, formula C_6H_5OH, has an hydroxyl group joined directly to an aromatic ring.



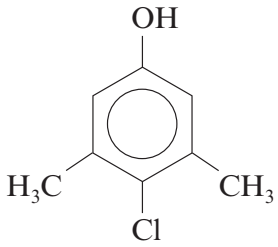
Phenol has many derivatives including 2-methylphenol.



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



TCP



Dettol

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

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

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

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

– End of passage –

Examiner only

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

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

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

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

.....

.....

.....

.....

.....

.....

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

.....

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

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

Calculate the atom economy of the reaction. [2]

.....

.....

.....

.....

Examiner only

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

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

.....

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

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

.....

.....

.....

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

.....

Total [15]

Total Section A [40]

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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.

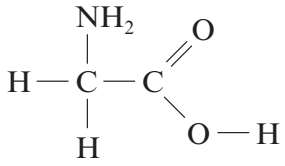
I. Write an equation for this reaction. [1]

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]

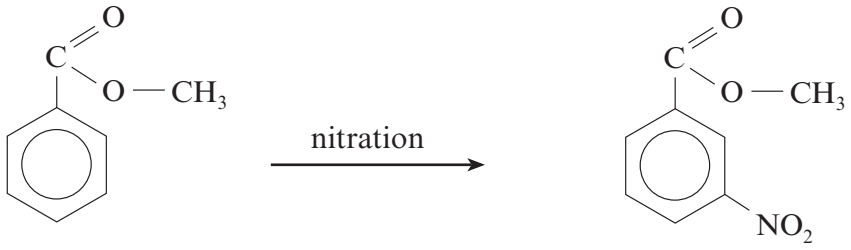
(iii) Proteins are natural polypeptides. Explain briefly what is meant by primary, secondary and tertiary protein structure. [3]

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]

WJEC
CBAC

GCE MARKING SCHEME

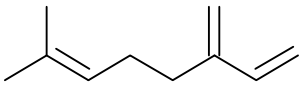
CHEMISTRY
AS/Advanced

SUMMER 2010

CH4

SECTION A

1. (a) (i) $C_{10}H_{16}$ (not shortened structural formula) [1]

(ii) 

[1]

(iii) I Compound that contains no double bonds / single bonds only [1]
(Accept contains maximum number of hydrogens)

II $C_{10}H_{16} + 3H_2 \longrightarrow C_{10}H_{22}$ [1]

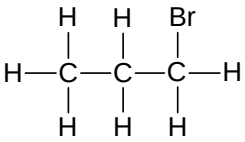
(accept structural formulae, consequential from (a)(i))

(iv) Moles $H_2 = \frac{8.96}{22.4} = 0.4$ [1]

4 double bonds [1]

(b) (i) Ethane (accept formula) [1]

(ii) $LiAlH_4$ [1]

(iii) 

[1]

(iv) (1-)Propyl ethanoate [1]

Total [10]

2. (a) In primary alcohols the –OH group is joined to a carbon atom bonded to two hydrogen atoms, in secondary alcohols the carbon atom is bonded to only one hydrogen. [1]

(b)

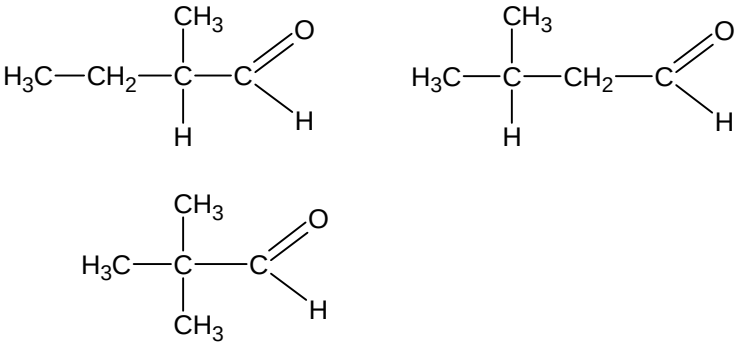
C	H	O
$\frac{68.1}{12}$	$\frac{13.7}{1.01}$	$\frac{18.2}{16}$
5.675	13.56	1.1375
4.99	11.92	1

[1]

Empirical formula = $C_5H_{12}O$ [1]

Formula mass, 88.1(2), is same as M_r, therefore molecular formula is $C_5H_{12}O$ [1]

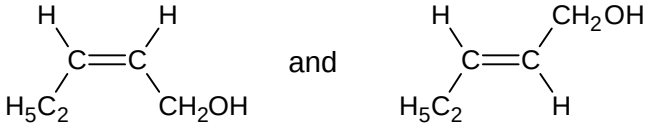
(c) (i) [1]



any one of three isomers

(ii) I C [1]

II [1]



(iii) Add Tollens' reagent / Fehling's solution [1]

A no reaction, **B** gives silver mirror / red ppt. [1]

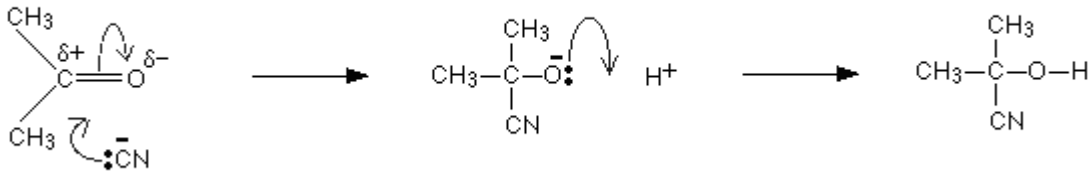
(iv) Add iodine in aqueous sodium hydroxide / KI and NaOCl [1]

C no reaction, **D** gives pale yellow ppt. [1]

(d) (i) Nucleophilic addition [1]

(ii) [3]

(1) (1)



(1)

Total [15]

3. (a) Iron(III) chloride / bromine water [1]
Purple solution / white precipitate [1]

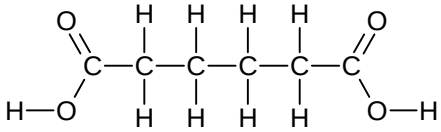
(b) In phenol anion formed is stabilised by delocalisation of the negative charge over the benzene ring (1)
In alcohol anion formed is not stabilised by delocalisation (1)
In carboxylic acids anion formed is stabilised by delocalisation of the negative charge over the two oxygen atoms (1)
Delocalisation is stronger in acid than in phenol (1)
Phenol loses H+ more easily than alcohol and carboxylic acid does so more easily than phenol (1)
(Accept diagrams)
max 4 marks [4]

(c) 4-chloro-3,5-dimethylphenol [1]

(d) Atom economy = $\frac{94.06 \times 100}{122.07}$ [1]

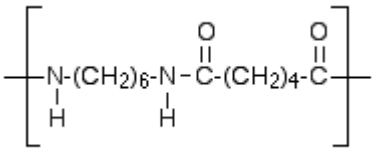
= 77% [1]

(e) [1]



(f) Hexane-1,6-diamine / 1,6-diaminohexane [1]

(g) [1]



(h) In addition polymerisation only the polymer is formed [1]
(Accept description e.g. monomers join together with no water loss)

In condensation polymerisation the polymer and a small molecule are formed [1]
(Accept description e.g. water molecule lost as monomers join together)
(Accept for 1 mark only water is eliminated during condensation polymerisation but not during addition polymerisation)

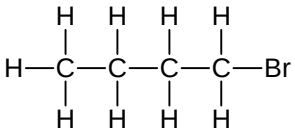
(i) Making aspirin / cellulose acetate / as an acylating agent [1]

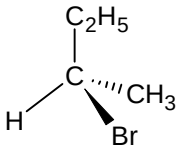
Total [15]

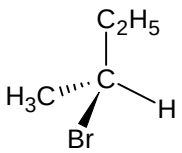
Total Section A [40]

SECTION B

4. (a) (i) [3]







(1) (1) (1)

(ii) Use a polarimeter to differentiate between isomers (1)
One will rotate plane of plane polarised light to the right and one to the left / opposite directions (1)
1-bromobutane will have no effect on plane polarised light (1) [3]

Accept use mass spectrometer / nmr spectroscopy to identify 1-bromobutane (1)
Answer gives peak present in 1-bromobutane that is not in other isomers (1)
(Accept converting to alcohols and carrying out iodoform test)

QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate [1]

(b) (i) I $C_2H_5Cl + NH_3 \longrightarrow C_2H_5NH_2 + HCl$ [1]

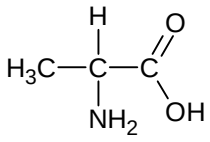
II Nucleophilic substitution [1]

(ii) Nitrobenzene (1)
Tin and concentrated hydrochloric acid (1) [2]

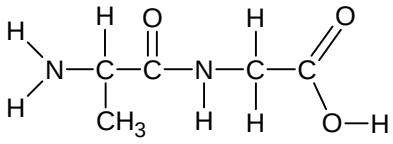
(iii) Sodium nitrite and hydrochloric acid, (1)
under 5 ºC (1)
No change phenylamine, bubbles (of nitrogen) with ethylamine (1)

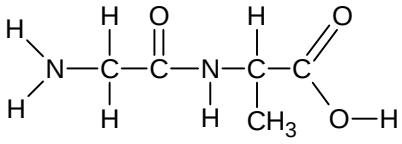
Accept alternative – bromine (1), aqueous (1), white ppt with phenylamine, no change with ethylamine (1)
[3]

(c) (i) [1]



(ii) [2]





(iii) Primary structure is the amino acid sequence (1)
Secondary structure is the folding / coiling / twisting of the primary structure (held by hydrogen bonding) (1)
Tertiary structure is the overall folding of the chain held by interactions (e.g. disulphide bridges, ionic bonding) between more distant amino acids / 3D structures (1) [3]

Total [20]

5. (a) Planar molecule (1)
each carbon bonded covalently to 2 other carbons and 1 hydrogen.(1)
Sideways overlap of p-orbitals. (1)
Leading to delocalised π – bonds. (1)
above and below plane of molecule (1)
(Maximum 4 marks for bonding)

Alkenes have localised double bond /greater electron density /
attract electrophiles more readily (1)
In benzene stable delocalised system would be disturbed / has extra delocalisation energy / reacts by substitution (1)
[6]

QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning (1)
Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1) [2]

(b) (i) Benzene is too hazardous / methylbenzoate is less toxic [1]

(ii) The product is crude / impure [1]

(iii) Add crystals to minimum amount of hot ethanol (1)
Filter if necessary and leave to cool (1)
Filter and dry (in air) (1) [3]

(iv) Take a melting point and compare it with a book value [1]

(v) $\frac{2.75}{1.1} = 2.5\ cm^3$ [1]

(vi) Moles methylbenzoate = $\frac{2.75}{136} = 0.0202$ (1)

Moles methyl 3-nitrobenzoate = $\frac{270}{181} = 0.0149$ (1)
% yield = 73.8 % (1) [3]

(vii) I Electrophilic substitution [1]

II NO_2^+ [1]

Total [20]

Total Section B [40]

Surname	Centre Number	Candidate Number
Other Names		2

WJEC CBAC

GCE A level

1094/01

CHEMISTRY CH4

P.M. WEDNESDAY, 15 June 2011

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	**Question**	**Mark**
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIAL

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.

Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

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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]

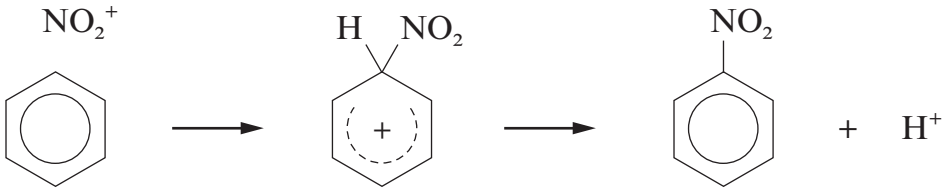
.....

(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]

.....

.....

Examiner only

(c) Explain why benzene compounds tend to react by electrophilic **substitution** rather than undergo electrophilic addition. [2]

(QWC) [1]

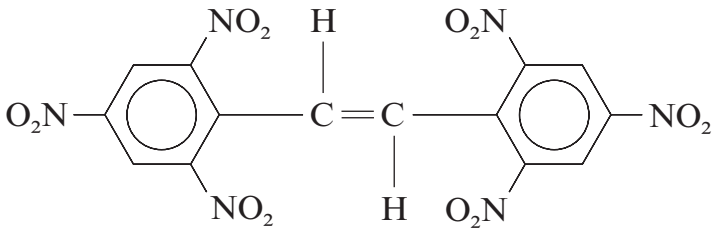
.....

.....

.....

.....

(d) Many explosives contain nitro-groups. The explosive hexanitrostilbene (HNS)



hexanitrostilbene

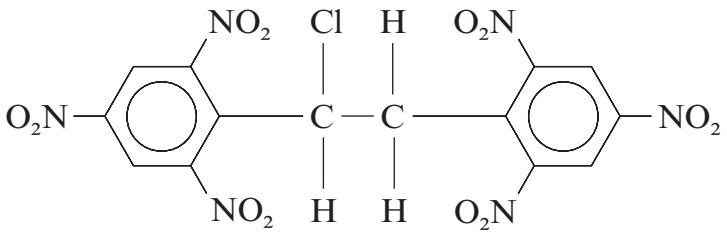
has been used to separate different sections in space rockets and for seismic experiments on the Moon.

(i) HNS is the E-isomer of a pair of E-Z isomers. State why HNS has both E- and Z-isomers. [1]

.....

.....

(ii) The manufacture of HNS is believed to proceed via compound **R**.



compound **R**

I Compound **R** contains a chiral centre. Identify the chiral centre in the formula of compound **R** by using an asterisk (*). [1]

Examiner only

II Compound **R** exists as two enantiomers. Explain what is meant by the term *enantiomers* and how these affect plane-polarised light. [2]

.....

.....

.....

III State the type of reaction that occurs when compound **R** is converted to HNS by the use of a suitable base. [1]

.....

Total [13]

1094 010005

Examiner only

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

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

.....

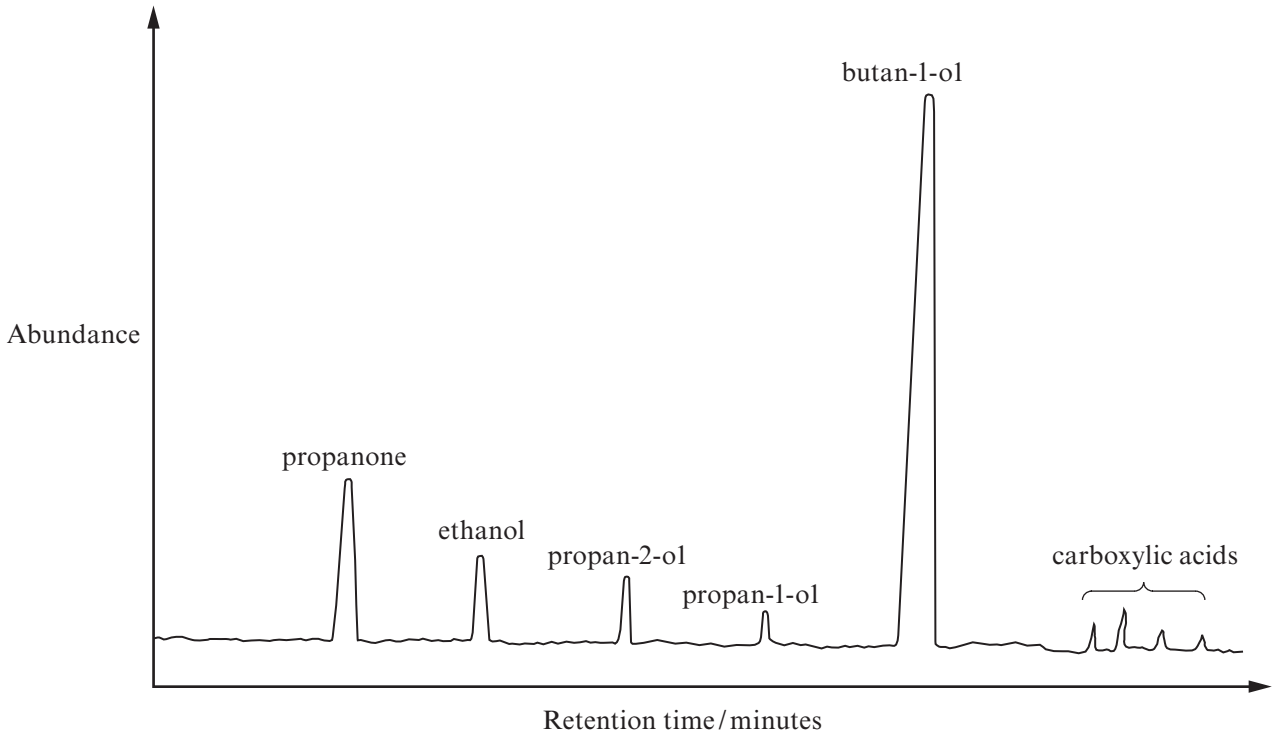
(ii) The infrared spectrum of butanal shows an absorption at 1731 cm^{-1}.
State which bond in butanal is responsible for this absorption and explain how the intensity of this absorption changes as the reduction proceeds. [2]

.....

.....

.....

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



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

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

....

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

.....

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

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

Explanation .....

.....

.....

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

.....

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

.....

.....

.....

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

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

.....

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

.....

Total [12]

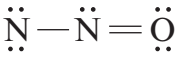
Read the passage below and then answer parts (a)-(g) in the spaces provided.

3.

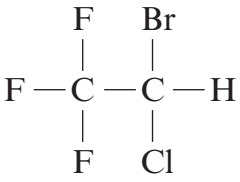
Anaesthetics

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.

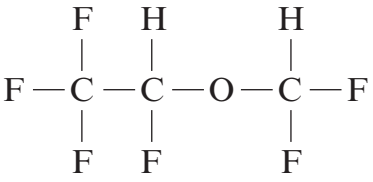
The first demonstrations of anaesthesia were in the late 1840s when Morton, in the USA, used ethoxyethane, and Simpson, in Scotland, used chloroform (trichloromethane). Later that century nitrous oxide, N_2O, was successfully used. In more recent times, up to about 1960, the most commonly used anaesthetics 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.



nitrous oxide

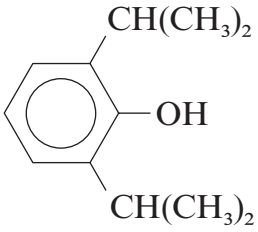


halothane

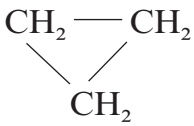


desflurane

ethoxyethane

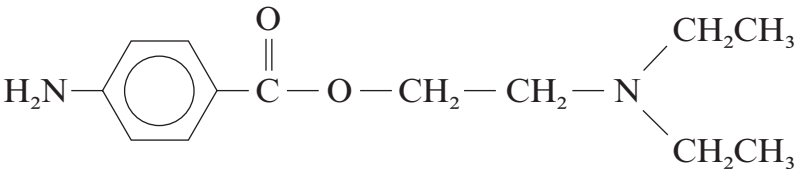


propofol

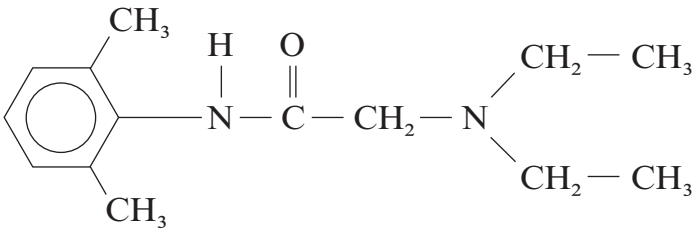


cyclopropane

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.

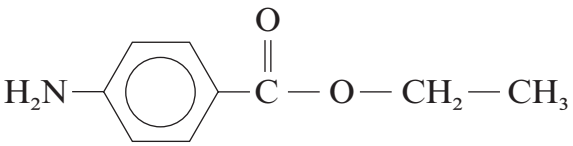


procaine



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 –

Examiner only

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

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

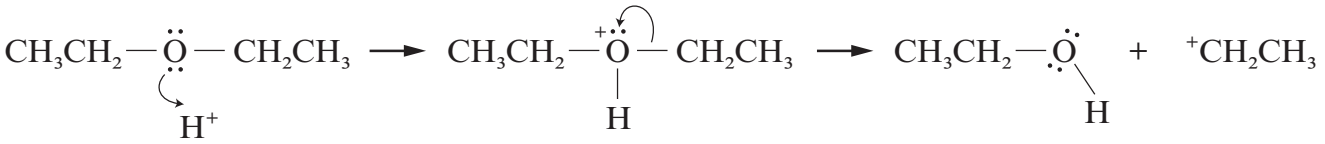
Nitrogen monoxide is a reactive molecule that contains an unpaired electron.
State the general name for species that contain an unpaired electron. [1]

.....

(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]

.....

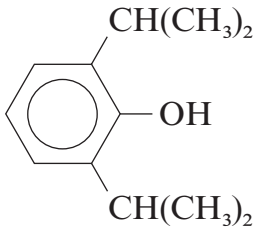
.....

.....

Examiner only

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

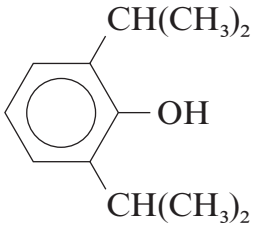
(i) State what would be seen if a few drops of iron(III) chloride solution were added to a solution of propofol in a suitable solvent. [1]



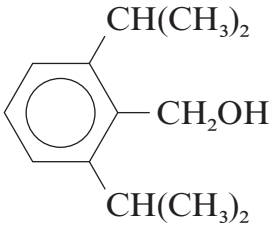
propofol

.....

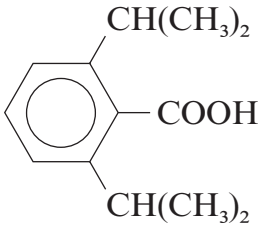
(ii) The formulae of propofol, compound **L** and compound **M** are shown below.



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]

.....

Examiner only

(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]

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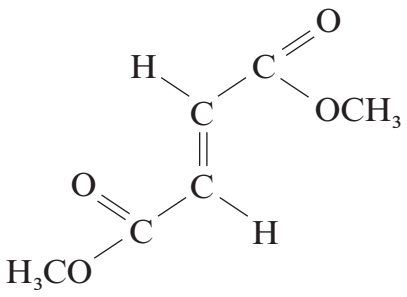
SECTION B

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

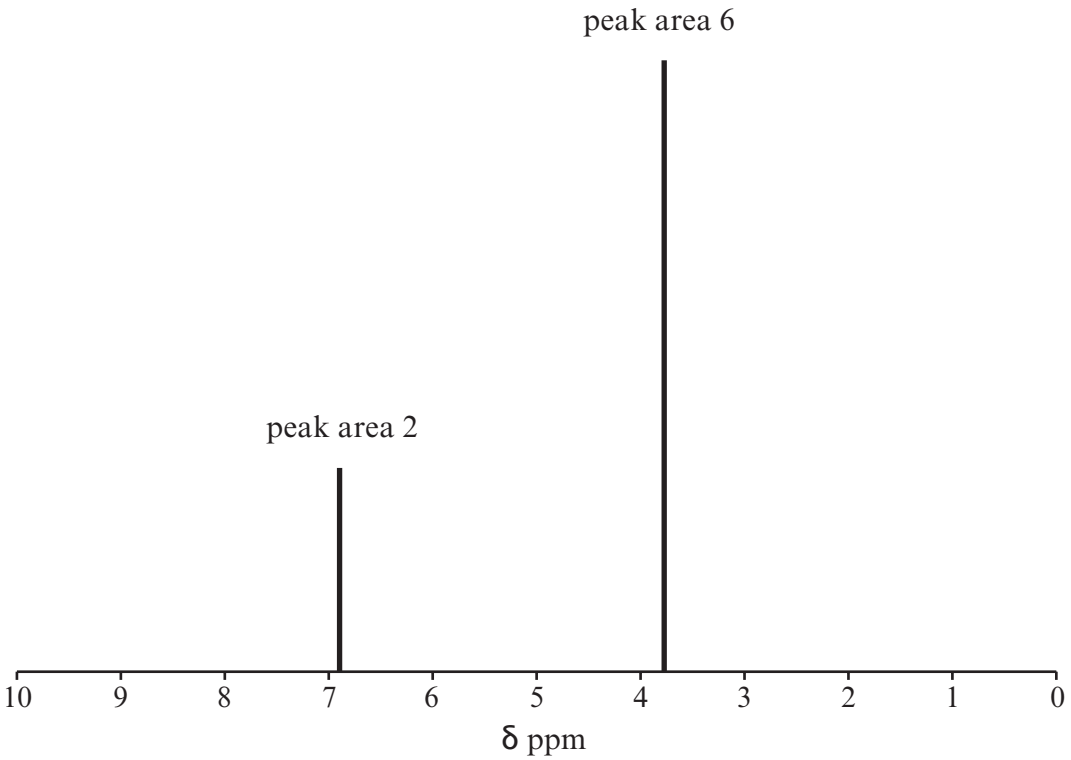
4. *(a)* In 2009 a man received compensation after he received chemical burns from a compound used as an antifungal agent in an imported leather sofa. The compound causing this problem was the ester dimethyl fumarate (DMF).



DMF

(i) DMF is one of a pair of E-Z stereoisomers. State what is meant by *stereoisomerism* and draw the displayed formula of the other stereoisomer of DMF. [2]

(ii) The NMR spectrum of the ester DMF is shown below.



The hydrolysis of dimethyl fumarate produces the dicarboxylic acid, fumaric acid. Describe how the NMR spectrum of fumaric acid would be different from the NMR spectrum of dimethyl fumarate.
Your answer should identify the peaks involved and include reasons for any changes that occur. You should also identify any NMR signal that does not change and the reasons for this. [5]

(QWC) [1]

(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.

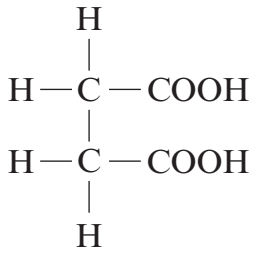
$$2CO_2 + \underset{M_r\,180}{C_6H_{12}O_6} \longrightarrow \underset{M_r\,116}{2C_4H_4O_4} + 2H_2O$$

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.

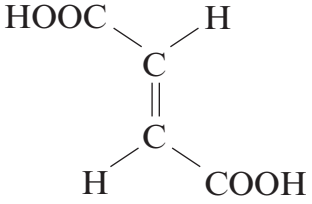
I One of these acids is ethanoic acid.
Outline any **one** other reaction that produces ethanoic acid.
Your answer should include
- the name of your starting material,
- any other reagent(s) used,
- the type of reaction occurring. [3]

II A small amount of butanedioic acid is also produced.



butanedioic acid

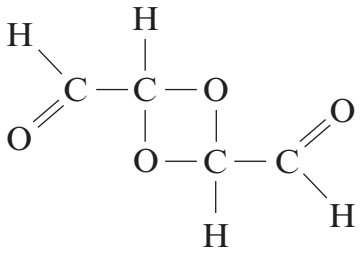
This acid can also be produced by the hydrogenation of the unsaturated acid, fumaric acid.



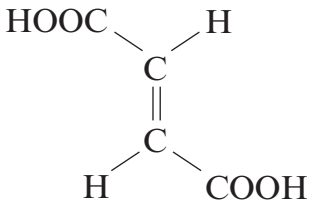
fumaric acid

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]

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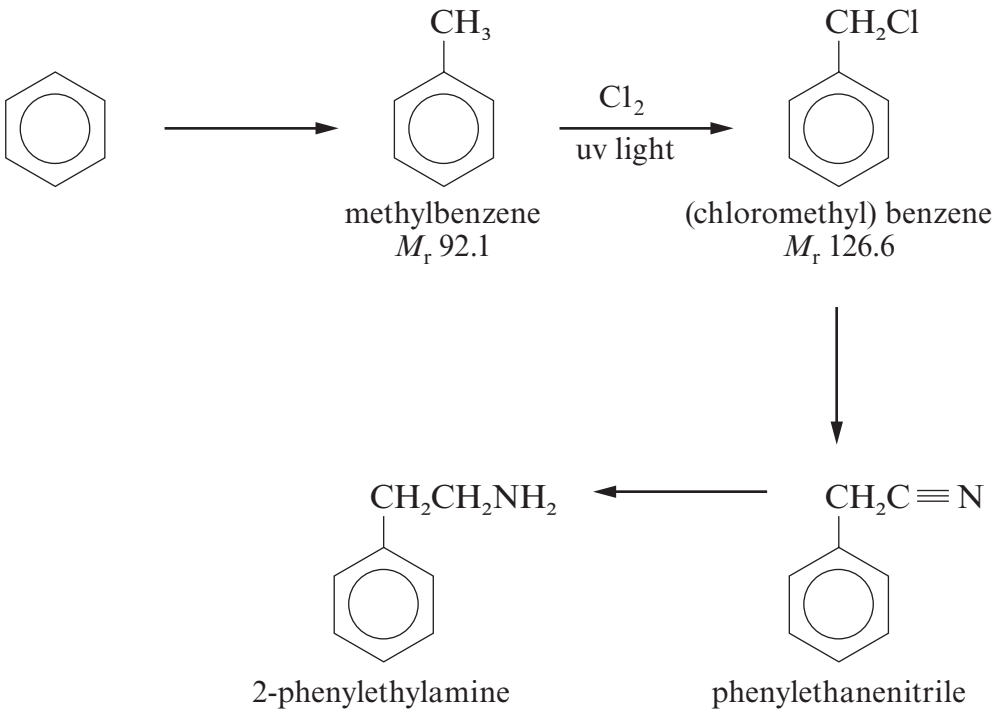
5. *(a)* 2-Phenylethylamine, present in chocolate, can be made from benzene in four stages.



(i) Give the equation, and the name of a suitable catalyst, for the Friedel-Crafts alkylation of benzene leading to methylbenzene. [2]

(ii) (Chloromethyl)benzene is produced by passing chlorine gas into methylbenzene in the presence of ultraviolet light. In practice the substitution by chlorine can proceed further giving (dichloromethyl)benzene and (trichloromethyl)benzene.
In order to prevent further chlorination the reaction is stopped when the increase in mass corresponds to (chloromethyl)benzene being produced.
You should assume that the other product, gaseous hydrogen chloride, is lost from the mixture.
In an experiment the following results were obtained.

Mass of flask	+	product	=	158.4 g
Mass of flask	+	methylbenzene	=	148.0 g
Mass of flask			=	120.4 g

Show that the increase in mass corresponds to the conversion of all the methylbenzene into (chloromethyl)benzene. [4]

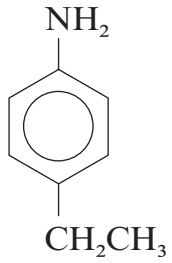
(iii) State the names of the reagents necessary to convert

I (chloromethyl)benzene to phenylethanenitrile, [1]

II phenylethanenitrile to 2-phenylethylamine. [1]

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

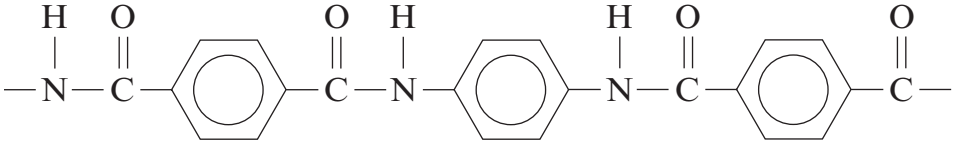
(c) State how both 2-phenylethylamine and its isomer 4-ethylphenylamine react with nitric(III) (nitrous) acid at 5°C.



4-ethylphenylamine

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

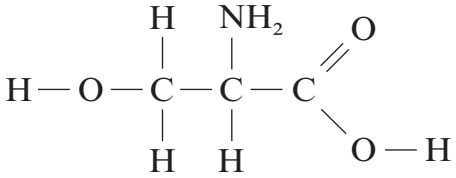
(d) Kevlar ® is a polyamide that is used in bullet-proof vests.



Kevlar ®

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

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



serine

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

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

(QWC) [1]

Total [20]

Section B Total [40]

WJEC
CBAC

GCE A level

1094/01-A

CHEMISTRY CH4
DATA SHEET

P.M. WEDNESDAY, 15 June 2011

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

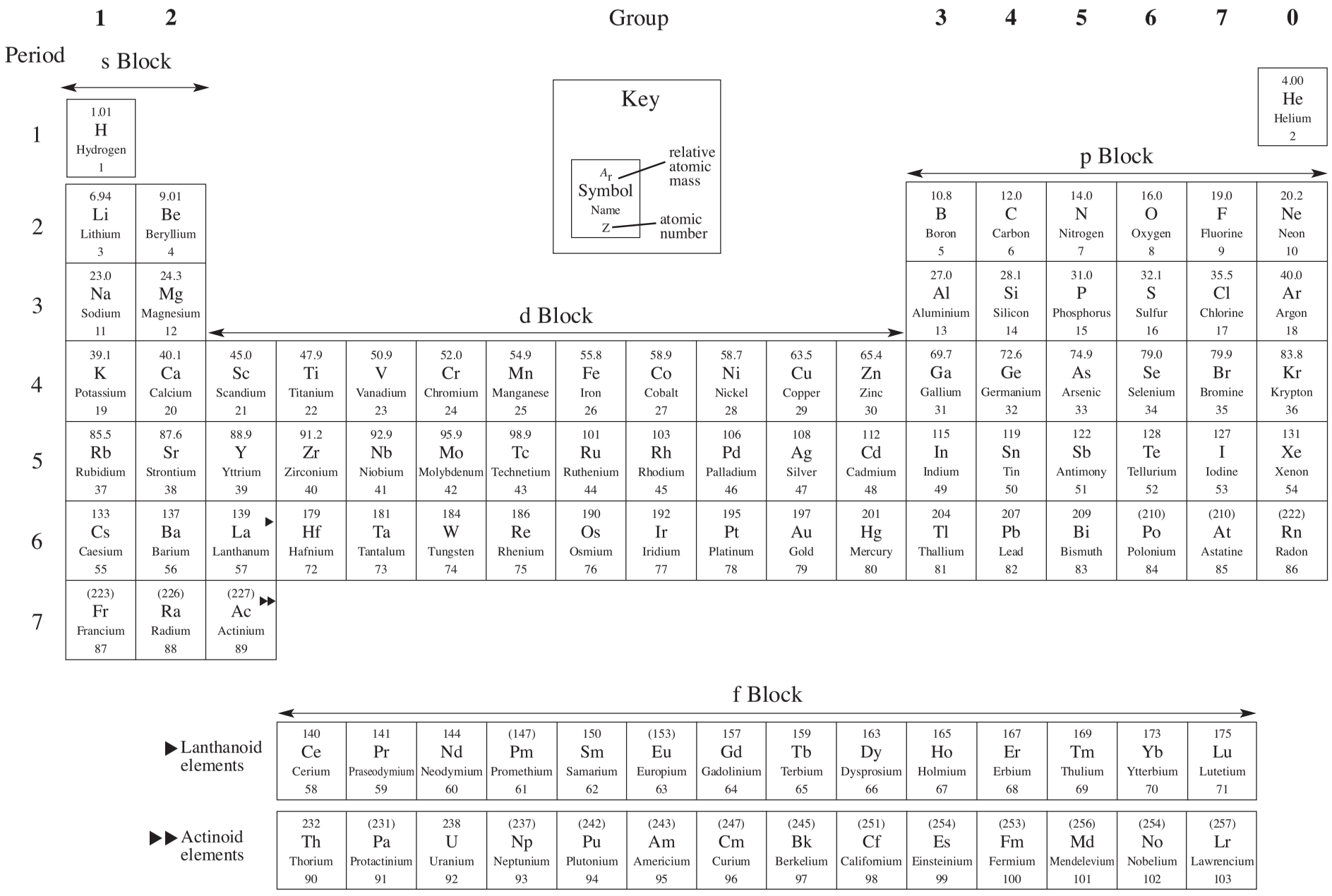
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
R—OH	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

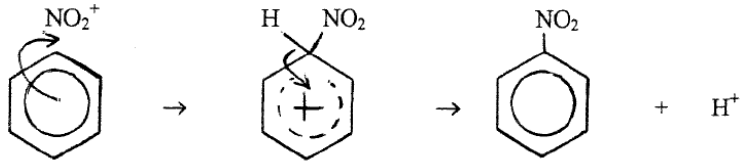
SUMMER 2011

CHEMISTRY - CH4

Q.1 (a) (i) Chromophore [1]

(ii) Yellow transmitted (or reflected) / other colours (e.g. blue and red) absorbed [1]

(b) (i)



(arrow must come from the bond) [1]

(ii) $C_3H_2NO_2$ [1]

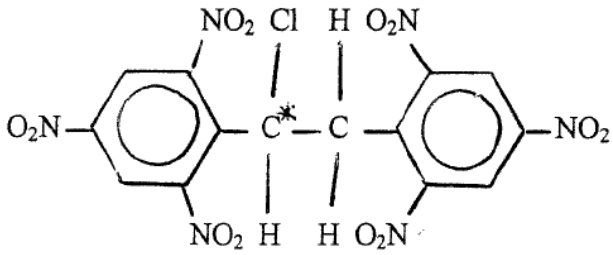
(iii) H_2SO_4 is losing a proton (to another species and becoming an HSO_4^- ion, acids are proton donors). [1]

(c) The benzene ring is more stable than an alkene because of its delocalised electron structure / π electron system / OWTTE (1)
If benzene underwent addition this would mean disrupting this stable electron system and this would require relative more energy / activation energy would be (much) higher. (1) [2]

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

(d) (i) There is no rotation about a double bond / each 'end' of the double bond has two different 'groups' attached to it [1]

(ii) I



[1]

II They are mirror image forms (1) that rotate plane polarised light in opposite directions (1) [2]

III Elimination [1]

Total [13]

Q.2 (a) (i) Sodium borohydride / sodium tetrahydridoborate(III) / lithium aluminium hydride / sodium and ethanol / zinc and ethanoic acid
(accept correct formulae) [1]

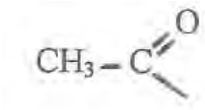
(ii) The absorption at ~ 1700 cm^{-1} is due to the C = O bond (1)
As the reaction proceeds the intensity of this absorption becomes smaller because the butanal is being used up / butan-1-ol does not contain a C = O bond (1) [2]

(b) (i) butan-1-ol > propanone > ethanol [1]

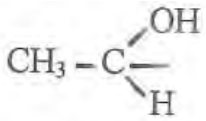
(ii) Propanone [1]

(iii) *Compounds* propanone / ethanol / propan-2-ol
Any two for one mark [1]

Explanation the compounds that give a positive iodoform test have to contain a



or the



grouping

[1]

(iv) So that a valid comparison can be made between results from other teams / OWTTE [1]
(do not accept 'fair test')

(c) There is a balance between the 'carbon' produced by burning and the 'carbon' absorbed by the plant (1)
When butan-1-ol is burnt carbon dioxide is produced, but this is used by plants / in photosynthesis to produce cellulose (1) [2]

(d) (i) $CH_3CH_2CH_2CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_2CH_2CH_3 + H_2O$ [1]

accept C_4H_2OH but not $C_4H_{10}O$ - functional groups must be present

(ii) (concentrated) sulphuric acid / H_2SO_4 / hydrogen chloride (gas) / HCl(g) [1]

do not accept H_2SO_4(aq) / HCl

Total [12]

Q.3 (a) (Free) radical [1]

(b) $2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$ [1]

(c) (i) It is providing a pair of electrons to bond to a proton / acting as a lone pair donor / proton acceptor [1]

(ii) I A process of boiling / evaporation and condensation without loss (of reactants) [1]

II By using an electrical heater / or a suitable heating bath / heating mantle - do not accept 'water bath' [1]

(d) Halothane would cause the most damage as it contains a weaker C-Cl / C-Br bond (1), which is broken in the upper atmosphere (1) (producing radicals that attack ozone).
Desflurane does not contain C-Cl / C-Br bonds, only the more stable C-F bonds. [2]

(e) (i) Purple colour / solution / complex - do not accept 'precipitate' [1]

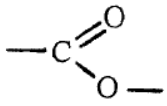
(ii) I

Compound	***Colour given with Universal Indicator paper***	***Reaction with sodium hydrogencarbonate solution***
propofol	yellow / orange	no reaction
compound **L**	~~~~~~~~~~~	~~~~~~~~~~~
compound **M**	orange / red	fizzing

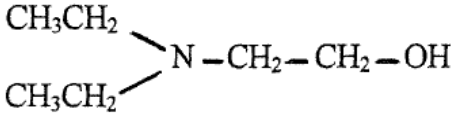
One mark for each correct column [2]

II Gas evolved turns ‘lime water’ milky [1]

(f) (i) [1]



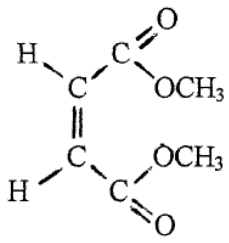
(ii) [1]



(g) It would melt at a lower temperature (than 89 ^{o}C) / below 89 ^{o}C (1)
and over a range of temperature / not a sharp melting temperature (1) [2]

Total [15]

Q.4 (a) (i) Stereoisomerism is where the compound has the same structural formula but whose atoms / groups take up different positions in space / in three dimensions (1)



[2]

(ii) The signal at 3.8 δ due to the methoxy protons (1) would disappear and be replaced by a signal at 11.0 δ (1) due to the O<u>H</u> protons (1). These protons would have peak area 2
(rather than peak area 6 for the methoxy protons) (1)
The signal at 6.9 δ would be (largely) unchanged (1) as the C –H bond is not affected by the hydrolysis of the ester. [5]

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

(iii) $C_6H_8O_4 \rightarrow 144$
113 is 31 less, could be CH_3O (1)
ion could be $C_5H_5O_3^+$ (1) [2]

(b) (i) Raw material prices become cheaper / reduce the reaction temperature / use a method where the % yield is increased [1]

(ii) Use a different (more economic) starting material / find a way of reducing the time taken for fermentation / effect an easier separation method.
Do not accept reference to increased amounts of enzyme /bigger batch. [1]

(iii) Number of moles of fumaric acid expected = 140 (1)

Actual number of moles of fumaric acid obtained = $\frac{13.0 \times 1000}{116}$ = 112 (1)

$$\% \text{ Yield} = \frac{112 \times 100}{140} = 80 \quad (1)$$

Alternatively

180 g / kg of glucose give 2 x 116 g / kg of fumaric acid (1)

$\therefore$ 1 g / kg of glucose gives $\frac{2 \times 116}{180}$ g / kg of fumaric acid

$\therefore$ 12.6 kg of glucose gives $\frac{2 \times 116 \times 12.6}{180}$ kg of fumaric acid = 16.2(4) kg (1)

$$\% \text{ Yield} = \frac{13.0 \times 100}{16.2} = 80 \quad (1)$$

[3]

(iv) I starting material (1) e.g. ethanol / ethanal OR ethyl ethanoate OR ethanoyl chloride

reagent (1)	$Cr_2O_7^{2-}$ / H^+	acid(aq) / base (aq) followed by acidification	water
type of reaction (1)	oxidation / redox	hydrolysis	hydrolysis

[3]

II platinum / nickel [1]

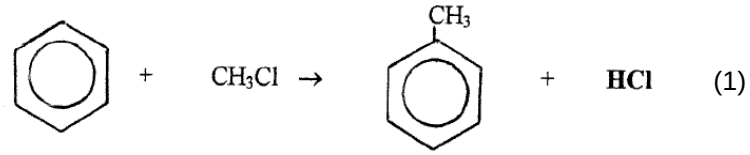
(c) e.g. Tollens reagent - silver mirror

OR 2,4 - dinitrophenylhydrazine - yellow/ orange / red precipitate

OR Fehling's / Benedict's reagent - brown / red precipitate [1]

Total [20]

Q.5 (a) (i)



(1)

catalyst - aluminium chloride (1) [2]

(ii) Mass of methylbenzene = 27.6 g (1)

Moles of methylbenzene = $\frac{27.6}{92.1}$ = 0.30(0) (1)

∴ 0.30 mole of $C_6H_5CH_2Cl$ should be made
this will have a mass of 0.30 x 126.6 = 38.0 g (1)

∴ Mass of flask + product needs to be 120.4 + 38.0 = 158.4 g (1) [4]

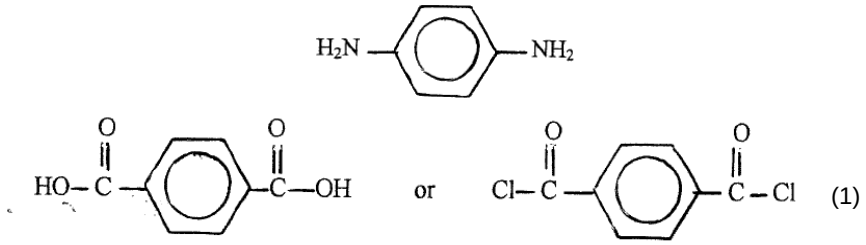
(iii) I potassium cyanide [1]

II lithium tetrahydridoaluminate(III) / lithium aluminium hydride (accept correct formulae) [1]

(b) The nitrogen atom is electron rich / has a lone pair (1) and will act as a proton acceptor / electron pair donor (1) [2]

(c) 2-Phenylethylamine reacts with nitrous acid giving an alcohol (1) and evolving nitrogen gas as bubbles (1)
4-Ethylphenylamine gives a diazonium compound (1) [3]

(d)



(1)

[2]

(e) (i) 2-amino-3-hydroxypropanoic acid [1]

(ii) Hydrogen bonding occurs because of the difference in electronegativity between hydrogen and oxygen / nitrogen(in O-H and N-H bonds), (1).
leading to polar covalent bonds / $\delta+$, $\delta-$ (1)
There are attractive forces between the oxygen or nitrogen of one molecule and the hydrogen atom bonded to an oxygen or nitrogen atom of another molecule (1) [3]

(Marks can be obtained from a suitable diagram)

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

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY CH4

A.M. WEDNESDAY, 13 June 2012

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	**Question**	**Mark**
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIAL

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.

Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

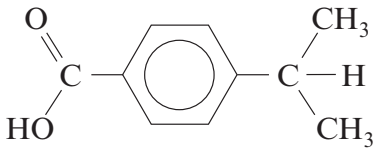
You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

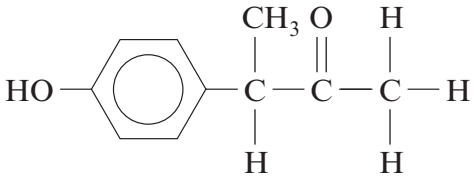
SECTION A

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

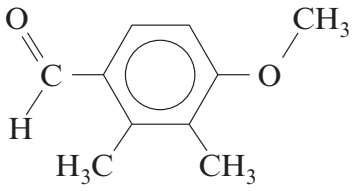
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



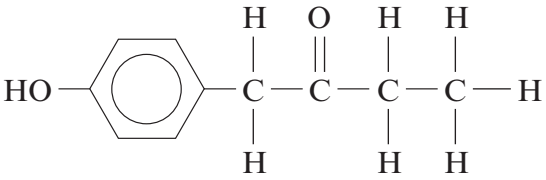
compound **W**



compound **X**



compound **Y**



compound **Z**

(a) Draw an **ester** which is an isomer of the compounds above. [1]

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

(i) Identify which compound can exhibit optical isomerism. ..... [1]

(ii) Indicate the chiral centre in this molecule by labelling it with an asterisk (*). [1]

(iii) State how the two enantiomers of this compound can be distinguished. [1]

.....

.....

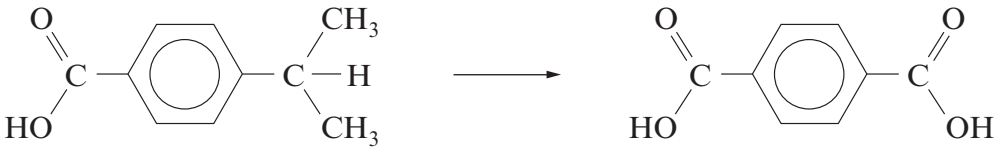
.....

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

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

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

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



compound **W**

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

(i) Give the reagent(s) and condition(s) required for this oxidation reaction. [2]

.....

.....

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

I. Give **two** differences between condensation polymerisation and addition polymerisation. [2]

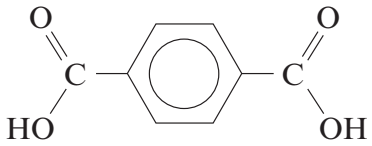
.....

.....

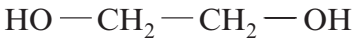
.....

Examiner only

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

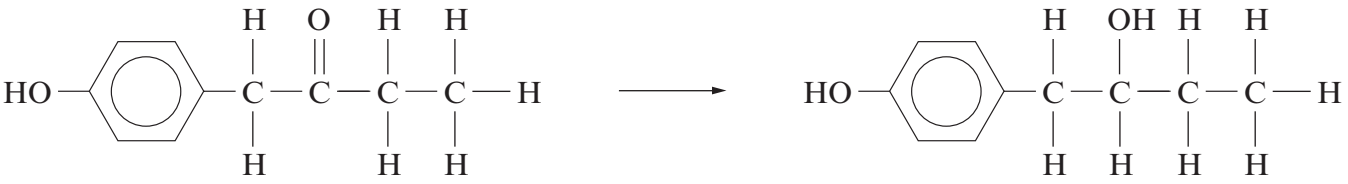


benzene-1,4-dioic acid
(terephthalic acid)



ethane-1,2-diol

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



compound **Z**

compound **V**

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

Reagent .....

Classification of reaction .....

(ii) Compound **V** will react with ethanoyl chloride.
Give the structure of a carbon-containing product of this reaction. [1]

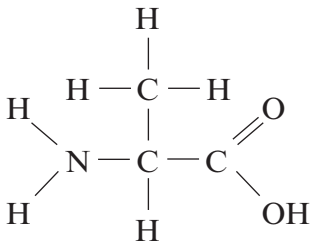
(iii) Compound **V** is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.
Give the structure of the carbon-containing species present in the resulting solution. [1]

Total [19]

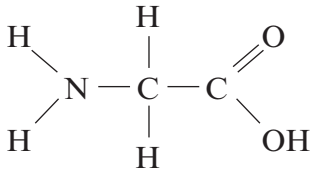
Examiner only

2. Proteins and polypeptides are natural polyamides built up from α-amino acids.

(a) Two naturally-occurring α-amino acids are alanine and glycine.

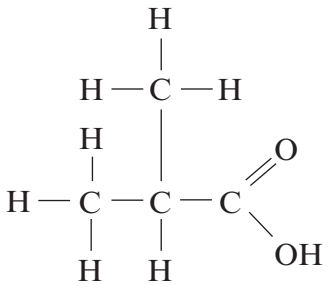


alanine
(2-aminopropanoic acid)



glycine
(2-aminoethanoic acid)

(i) Alanine *(2-aminopropanoic acid)* has a melting temperature of 258 °C whereas the similar compound 2-methylpropanoic acid melts at –46 °C.



2-methylpropanoic acid

Explain why the value for alanine is so much higher than that of 2-methylpropanoic acid. [2]

.....

.....

.....

(ii) Draw the **two** possible dipeptides that can form when one molecule of glycine combines with one molecule of alanine. [2]

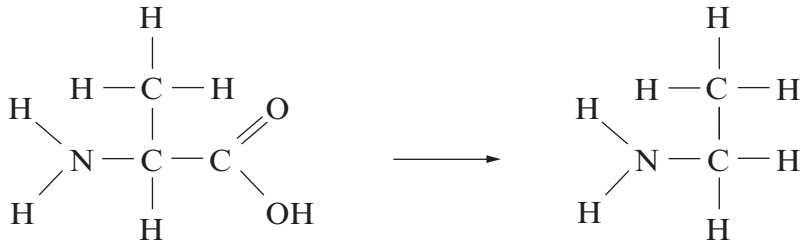
(iii) Circle the peptide linkage in **one** of your dipeptides. [1]

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

.....

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

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



Name the reagent required for this reaction. [1]

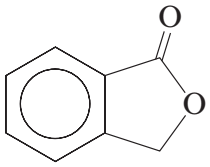
.....

Total [10]

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

Phthalides

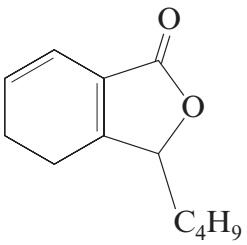
Phthalides are a family of compounds which are present in many plants, fungi and moulds. They are all based around the basic phthalide structure which has a benzene ring with a five-membered cyclic ester attached to it.



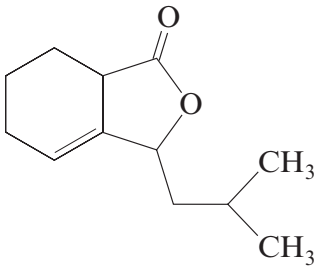
phthalide

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.

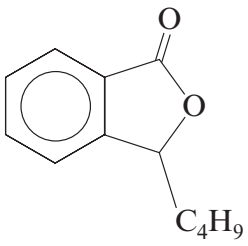
Some phthalides and their derivatives also act to enhance the flavour of food. In studies of celery, it was found that three particular compounds present in the plant had no flavour of their own, but enhanced the flavours of other foods when cooked together. These three were sedanenolide, sedanolide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



sedanenolide



sedanolide

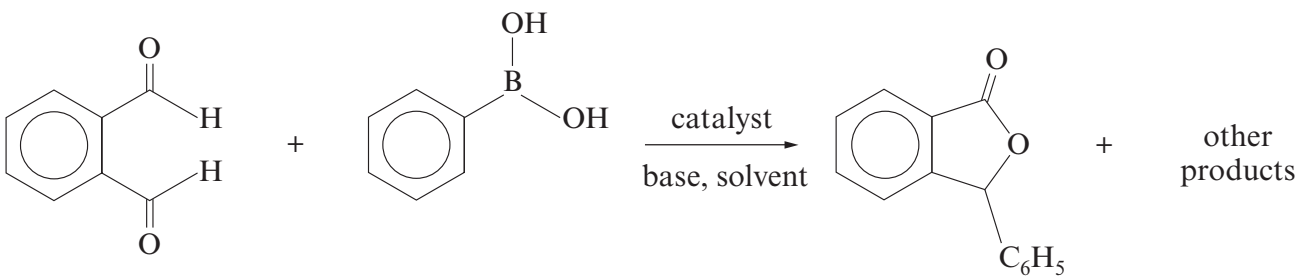


3-butylphthalide

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

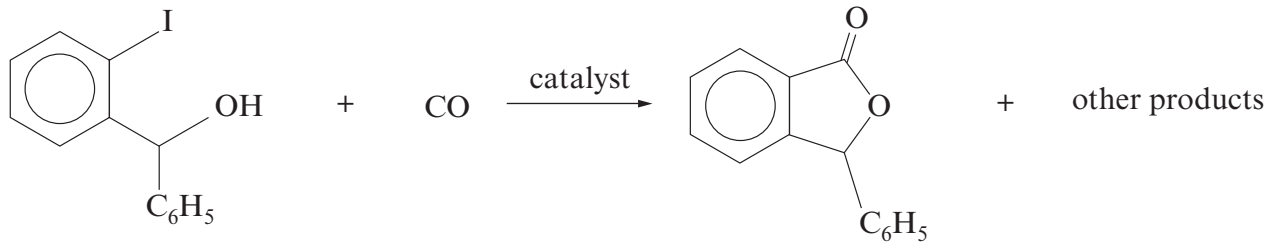


compound **Q**
M_r = 134

M_r = 122

phthalide **P**
M_r = 210

Route 2



compound **R**
M_r = 310

carbon monoxide
M_r = 28.0

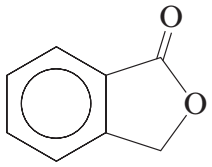
phthalide **P**
M_r = 210

– End of passage –

Examiner only

(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]



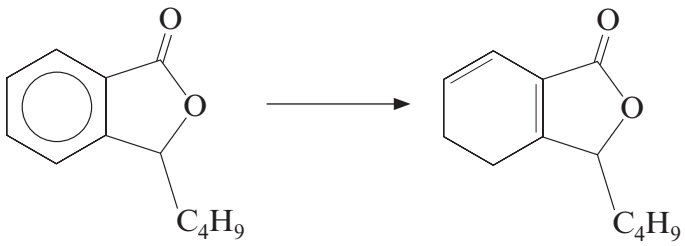
phthalide

(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]

.....

.....

.....

Examiner only

(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 .....

.....

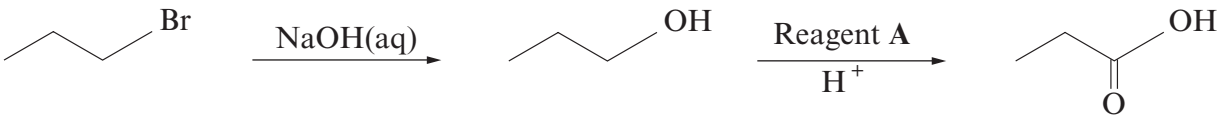
Total [11]

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 $^{1}_{1}H$ nuclear magnetic resonance spectrum.

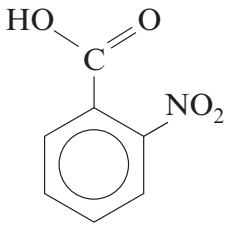
- A triplet at 1.0 ppm with an area of 3
- A singlet at 2.1 ppm with an area of 3
- A quartet at 4.0 ppm with an area of 2

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

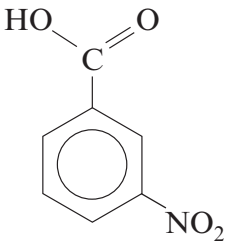
(QWC) [2]

Total [20]

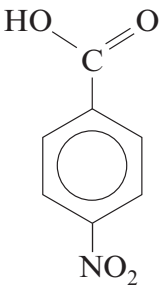
5. *(a)* Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



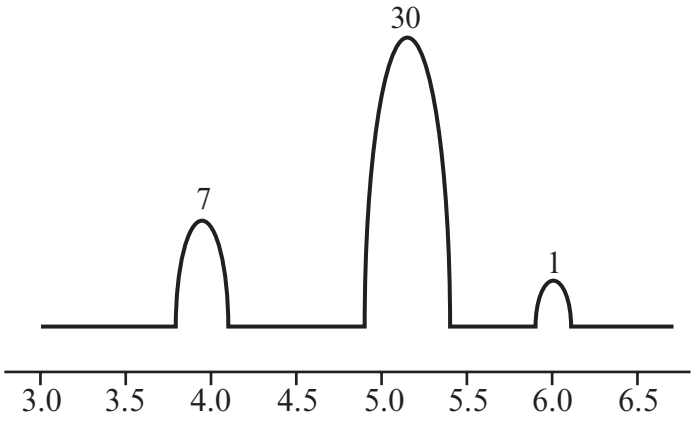
3-nitrobenzoic acid



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.

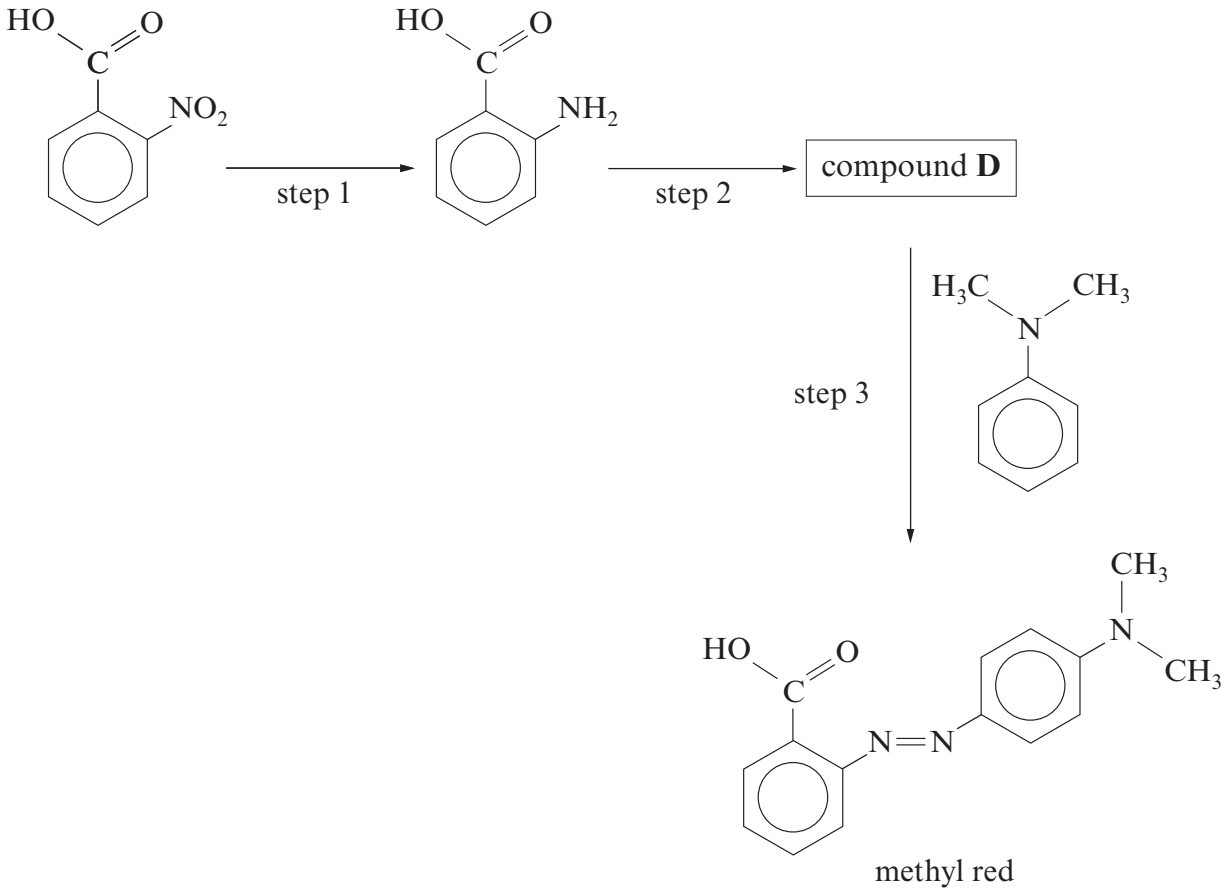
I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all. [1]

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]

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

A.M. WEDNESDAY, 13 June 2012

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

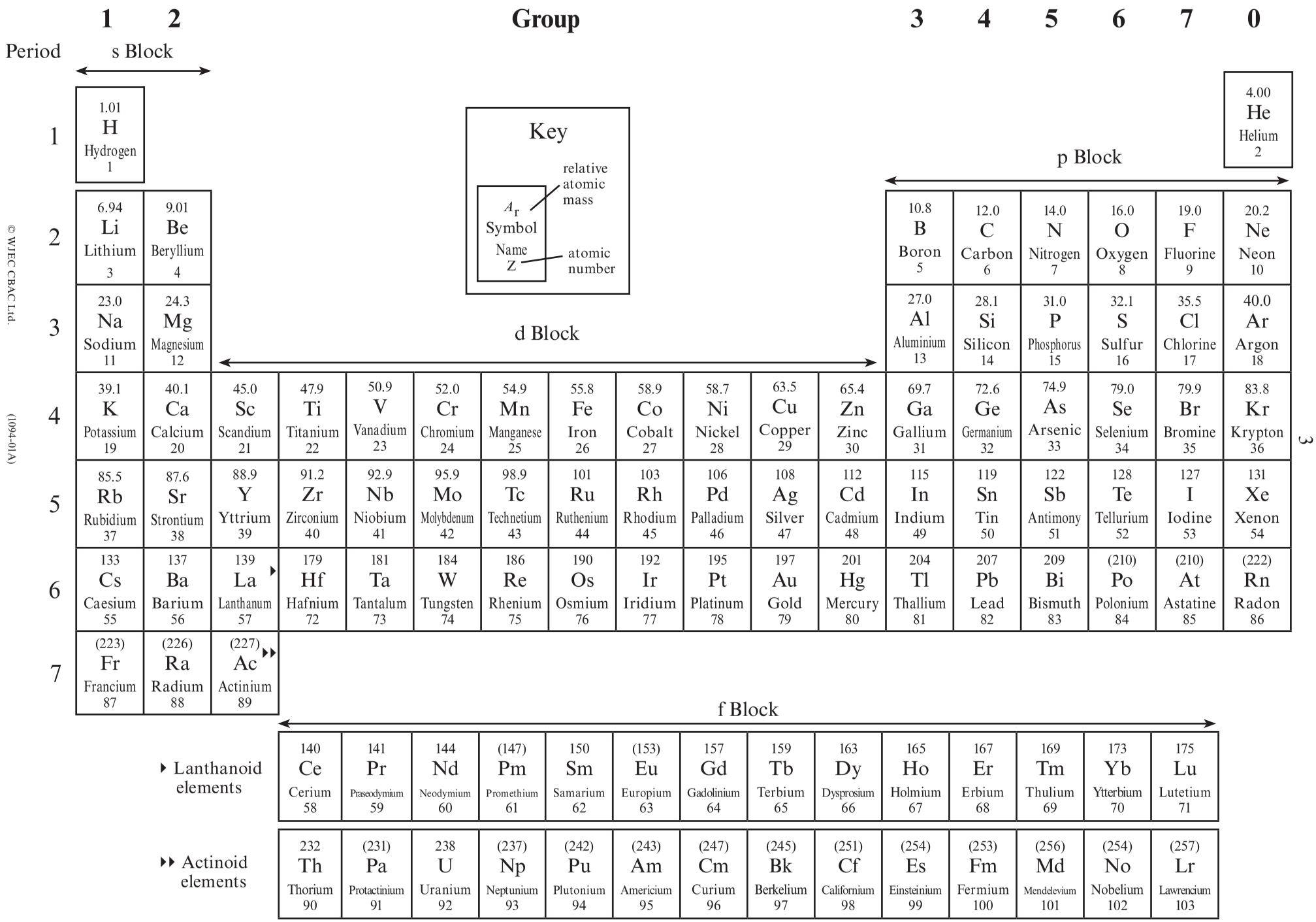
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

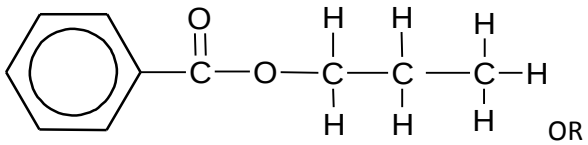
SUMMER 2012

CH4

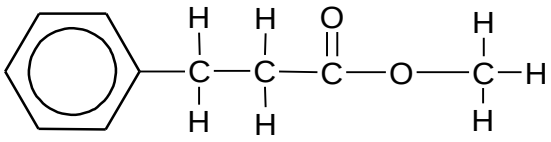
Question 1

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

Examples:

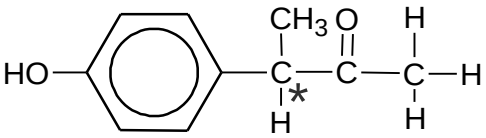


OR



(b) (i) Compound X [1]

(ii)



[1]

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

(c)

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

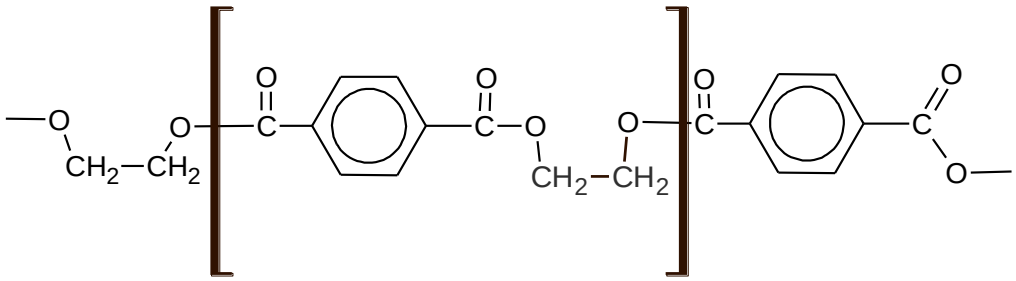
(*1 mark for each box*) [6]

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

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

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

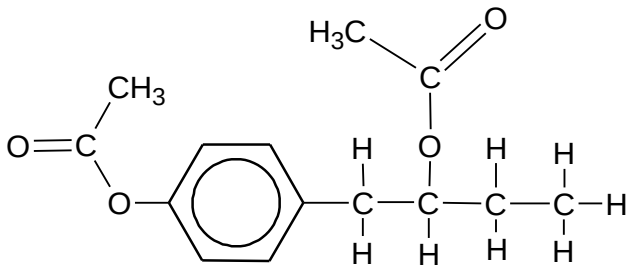
II.



[1]

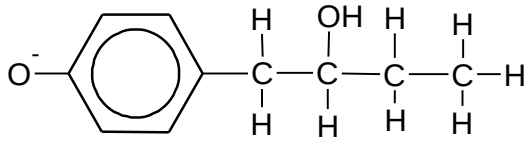
(e) (i) $NaBH_4$ / $LiAlH_4$ or name(1) Reduction (1) [2]
- ignore conditions unless $LiACH_4$ in water
- do not accept 'redox'

(ii)



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

(iii) [1]

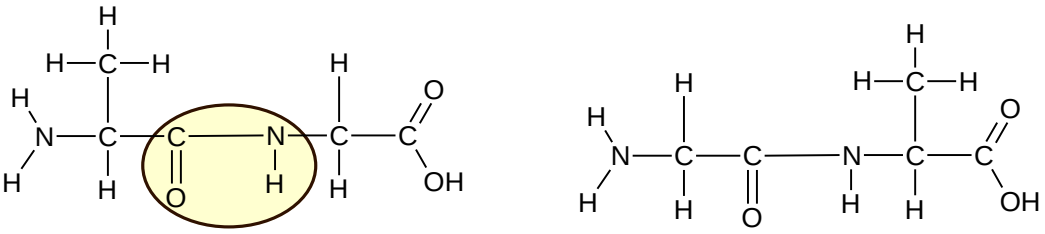


[19 marks]

Question 2

(a) (i) Alanine forms a zwitterion (1)
Forces between alanine molecules are ionic bonding (1)
Ionic bonding much stronger than hydrogen bonding / van der Waals (1)
Max 2 marks [2]

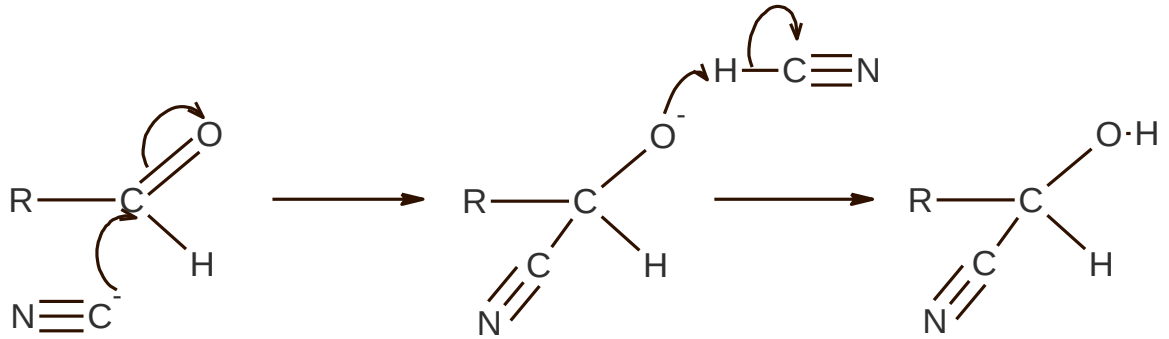
(ii) 1 mark for each correct structure [2]



(iii) 1 mark for correct identification of peptide link [1]

(b) Enzymes / Structural proteins / Hormones or specific example [1]

(c) 1 mark for arrows in first stage; 1 mark for correct intermediate; 1 mark for arrow giving gain of proton in second stage (from HCN or from H^+).



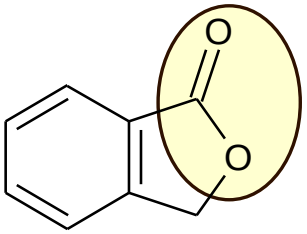
[3]

(d) Soda lime [1]

[10 marks]

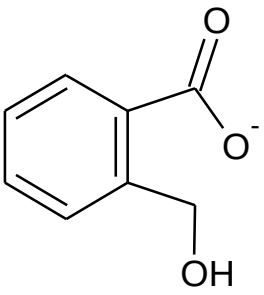
Question 3

(a) (i) [1]



Phthalide

(ii) [1]



(b) Distillation / Chromatography [1]

(c) Hydrogenation of 3-butyl phthalide removes a benzene ring (1)
Benzene ring is more stable than alkene/ Reference to delocalisation energy (1) [2]

(d) 62.1% [1]

(e) (i) Greater variety of different phthalides that can be produced [1]

(ii) Higher atom economy / less waste / carbon monoxide is toxic [1]
- do not accept references to yield

(f) Silver nitrate and ammonia / Tollen's reagent (1); Q = Silver mirror (1); R = No reaction (1)
OR 2,4,-DNP (1); Orange precipitate with Q (1); No reaction with R (1)
OR Fehling's solution (1); Orange solid with Q (1); No reaction with R (1) [3]

[11 marks]

Question 4

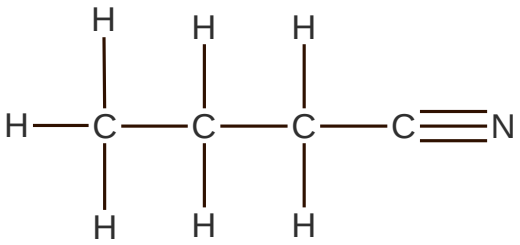
(a) (i) Nucleophilic substitution / Hydrolysis [1]

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

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

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

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



(1) [3]

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

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

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

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

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

[5]

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

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

[20 marks]

Question 5

(a) (i) (Concentrated) nitric acid / (concentrated) sulfuric acid / Temperature of 40-80°C
(*Any 2 = 1 mark; All 3 = 2 marks*)
Electrophilic substitution (1) [3]

(ii) I. Peak area is proportional to amount of substance (1)
Percentage = (30 / 38) x 100 = 79% (1)
(Can obtain both marks from correct percentage) [2]

II. 45 = $COOH^+$, 46= NO_2^+, 122 = $C_6H_4NO_2^+$ and 167 = $C_7H_5NO_4^+$.
(*Any 2 = 1 mark; All 4 = 2 marks*) [2]

(iii) I. Lower melting point / melts over a range [1]
II. 1 mark for each point.

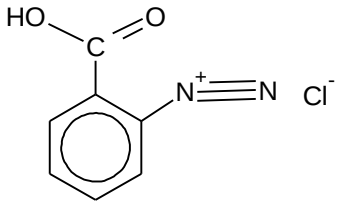
- Dissolve in the minimum volume
- Of hot water
- Filter hot
- Allow to cool
- Filter
- Dry residue under suction / in oven below 142°C

Max 4 marks [4]

QWC: legibility of text, accuracy of spelling, punctuation and grammar, clarity of meaning.[1]

(b) (i) Tin and concentrated hydrochloric acid [1]

(ii) Below 10°C (1)



(1) [2]

(iii) N=N double bond is chromophore (1)
Compound absorbs blue /green / complementary colours to red / all colours but red (1)
Remaining frequencies are transmitted, giving the red colour seen. (1)
Any 2 out of 3 [2]

(c) Nitrogen has a lone pair (1) which can accept a proton (1) [2]

[20 marks]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY – CH4

P.M. WEDNESDAY, 12 June 2013

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	**Question**	**Mark**
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIAL

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.

Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

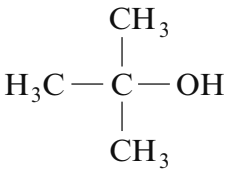
Examiner only

SECTION A

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

1. *(a)* In 2012 an off-licence in Derby was prosecuted for selling fake vodka.

(i) A report in the local paper stated that this 'vodka' was contaminated by 'tertiary butanol', the formula of which is shown below.



State the **systematic** name of this compound. [1]

.....

(ii) Analysis showed that the total alcohol content of a bottle of the fake vodka was 35%.
A gas-liquid chromatogram showed a mixture of alcohols to be present in the following proportions:

tertiary butanol	6 parts
methanol	8 parts
ethanol	86 parts

Calculate the percentage of ethanol by volume in the fake vodka. [1]

..... %

(iii) Tertiary butanol can be dehydrated in an elimination reaction to produce 2-methylpropene. Suggest a suitable dehydrating agent for this reaction. [1]

.....

Examiner only

(iv) 2-Methylpropene can be polymerised to give poly(2-methylpropene). Draw the repeating unit of the polymer. [1]

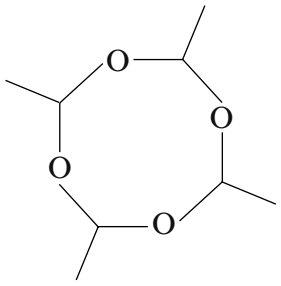
(v) Write the displayed formula of any isomer of tertiary butanol that contains a chiral centre. Identify the chiral centre by an asterisk (*). [2]

(vi) The main alcoholic compound of the fake vodka is ethanol. This can be oxidised to give ethanal.

I State the reagent(s) used to oxidise ethanol to ethanal in the laboratory. [1]

.....

II Ethanal can be polymerised to 'metaldehyde', $(CH_3CHO)_4$, which is used to kill slugs.



Use the Data Sheet to describe how the infrared spectrum of 'metaldehyde' will differ from the infrared spectrum of its monomer, ethanal, giving the absorption values and the bonds involved. Reference to C—H bonds is not required. [2]

.....

.....

.....

1094 010003

Examiner only

(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]

Examiner only

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]

.....

.....

.....

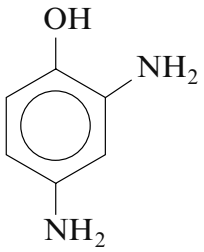
(b) 2,4-Dinitrophenol is a yellow solid that is an inhibitor of ATP production in cells. As a result it has been sold as an aid to slimming, in spite of it being a dangerous and unlicensed product.

(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'.



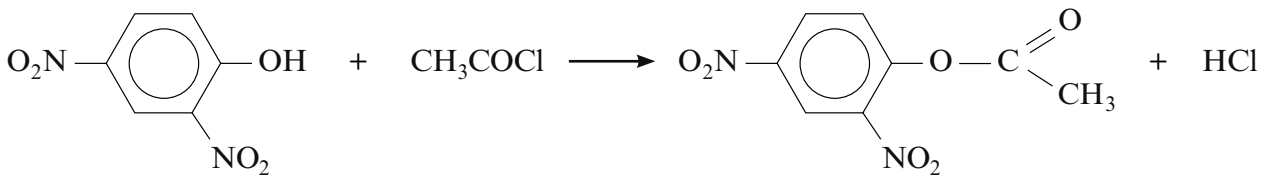
amidol

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

.....

Examiner only

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

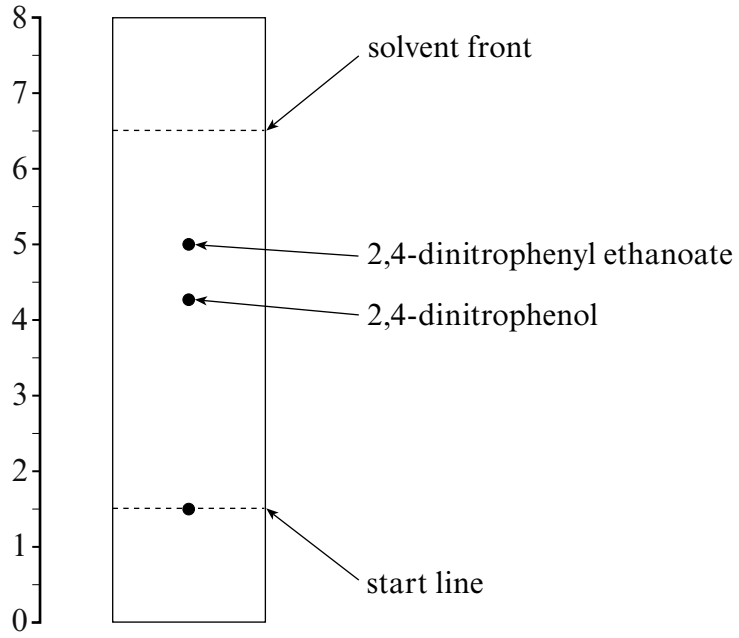


M_r = 184 M_r = 226

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]

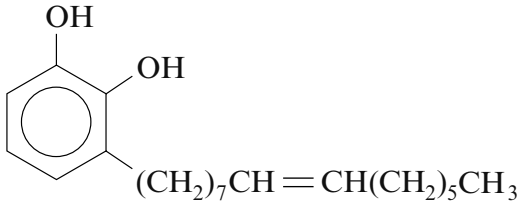
.....

.....

.....

Examiner only

(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]

.....

.....

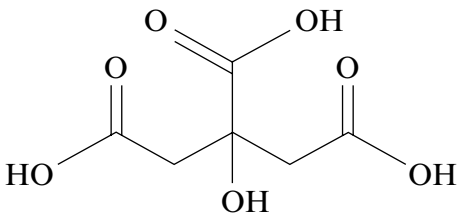
.....

Total [12]

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

Citric acid – its production and chemistry

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



$M_r = 192$

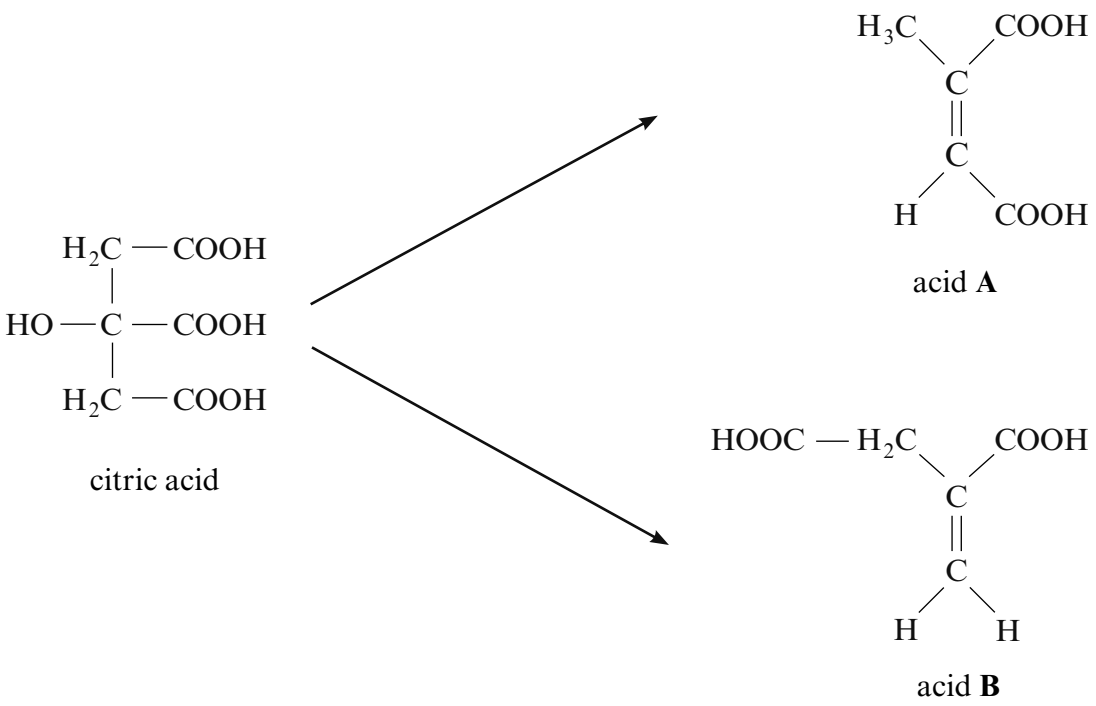
citric acid

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

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

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

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

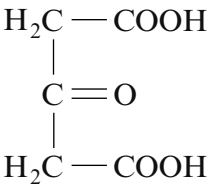


citric acid

acid **A**

acid **B**

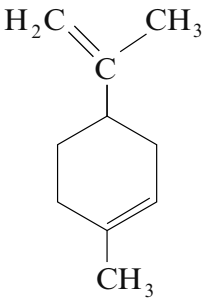
When citric acid is treated with concentrated sulfuric acid, acid **C** is formed.



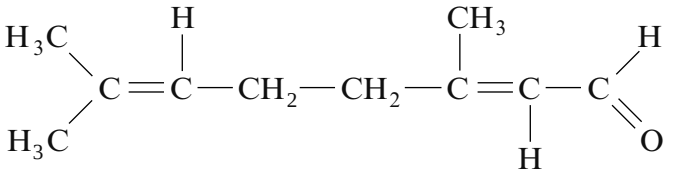
15

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 –

Examiner only

(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]

.....

.....

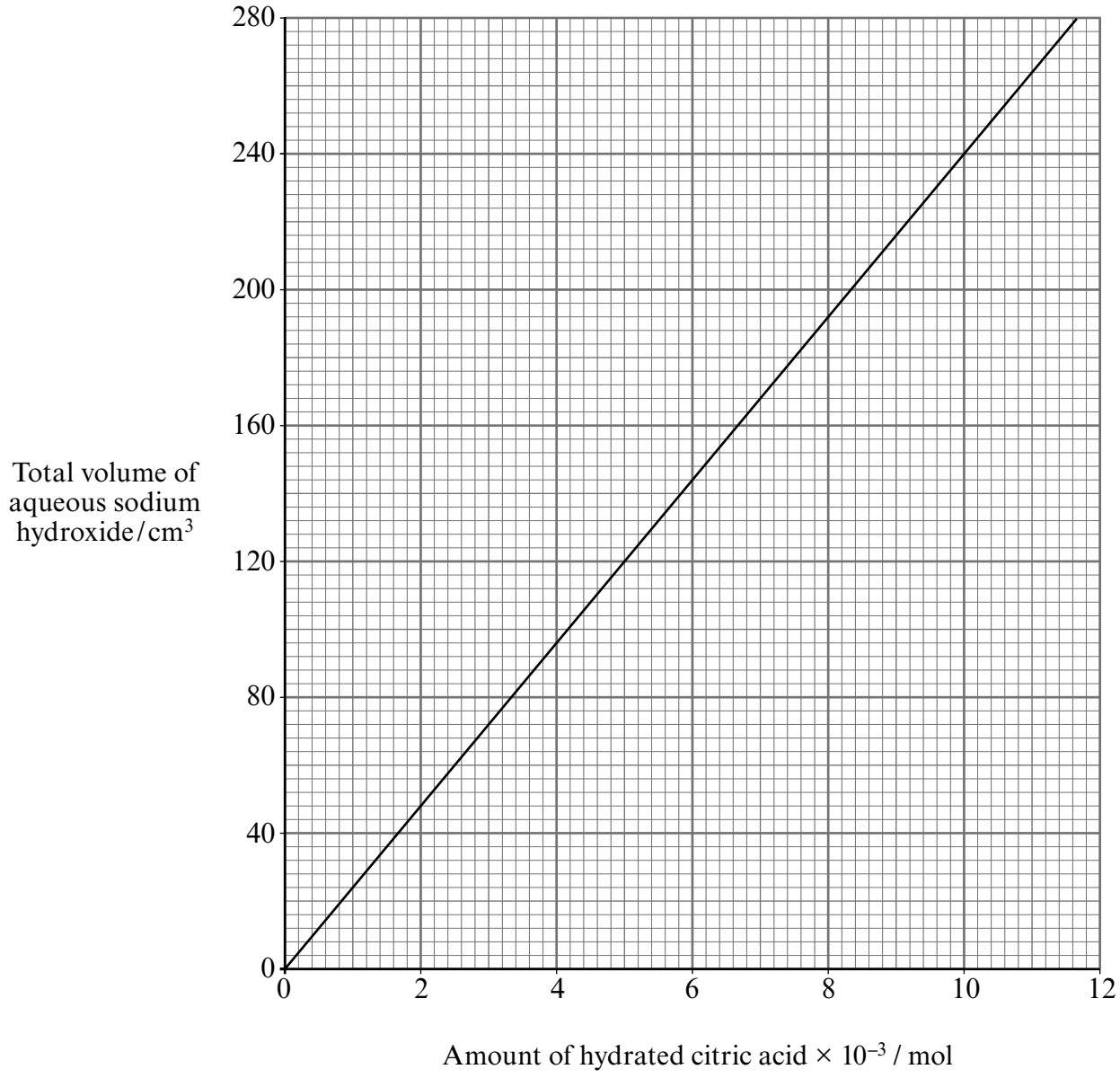
(b) Citric acid occurs in two forms – an anhydrous form and a hydrate.
Some students were given samples of the **hydrated** form of this tribasic acid and were asked to find its relative molecular mass by a titration with aqueous sodium hydroxide, using a suitable indicator to monitor complete neutralisation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

Examiner only



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

.....

.....

Examiner only

(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

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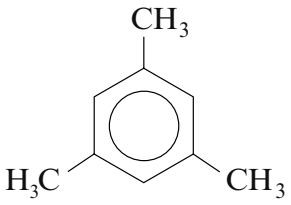
SECTION B

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

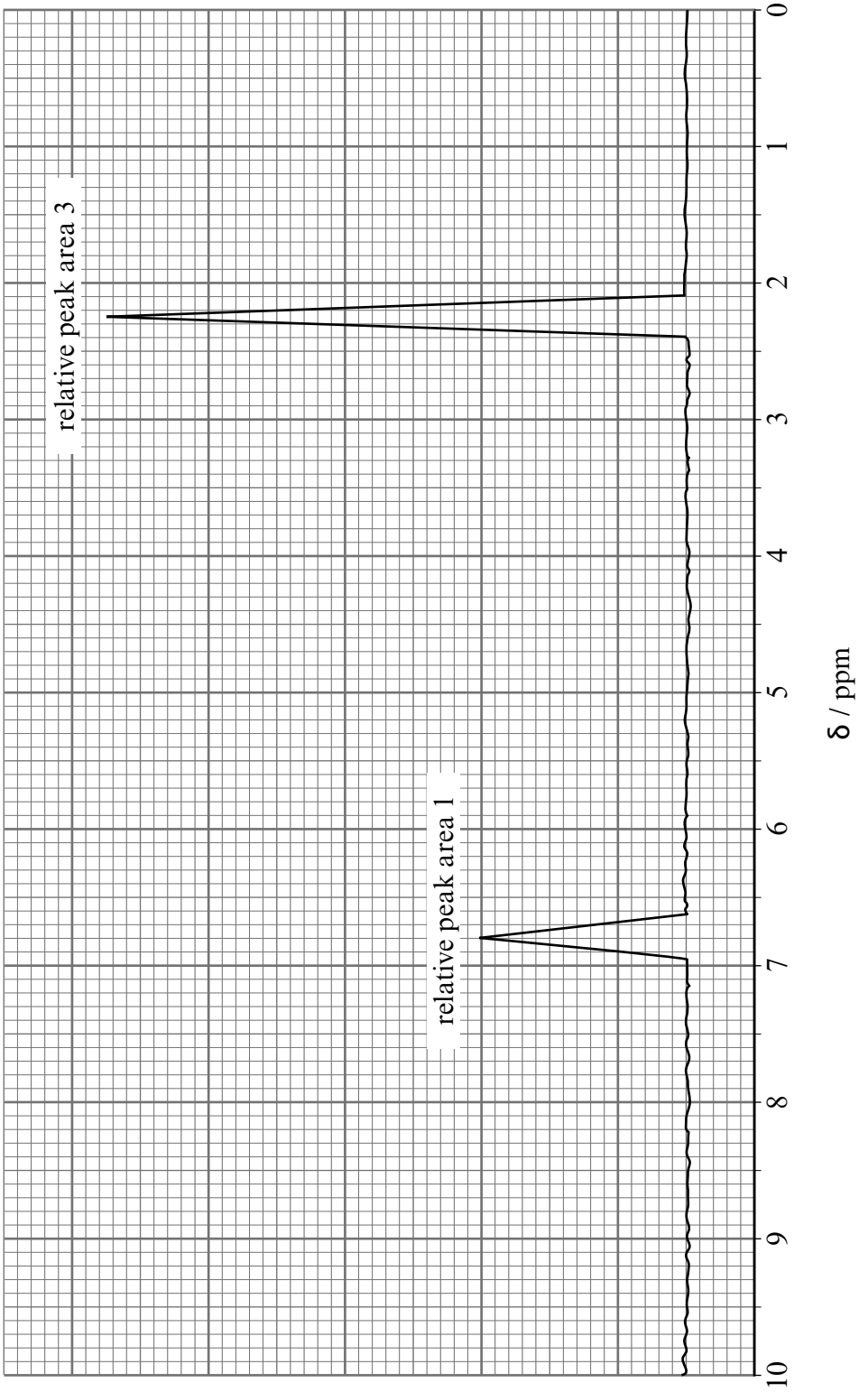
4. *(a)* Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions. [6]
QWC [2]

(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]

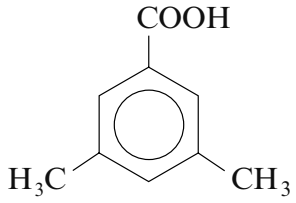
(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.



(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

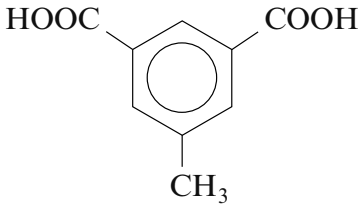
(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



melting temperature 172 °C

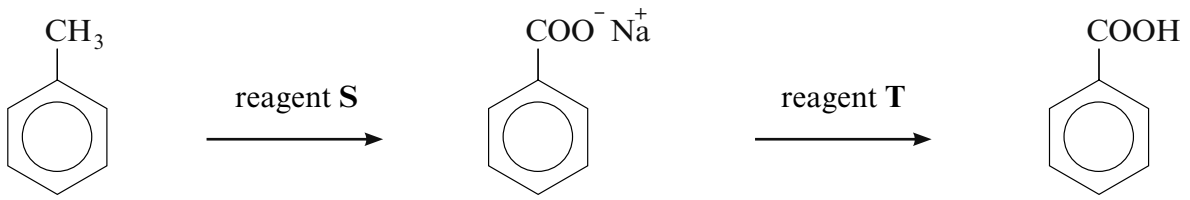
Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water. [4]

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



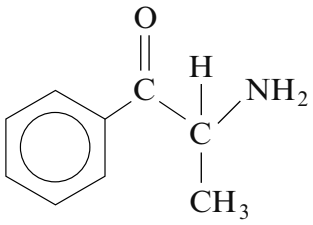
By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol. [1]

(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**.

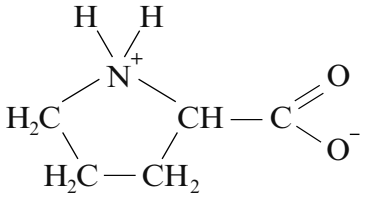
- It contains a peptide linkage.
- It can be hydrolysed by aqueous sodium hydroxide giving primary aromatic amine **M** as one of the products.
- Primary aromatic amine **M** reacts with nitric(III) acid (nitrous acid) to give a phenol with the molecular formula C_7H_8O.

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

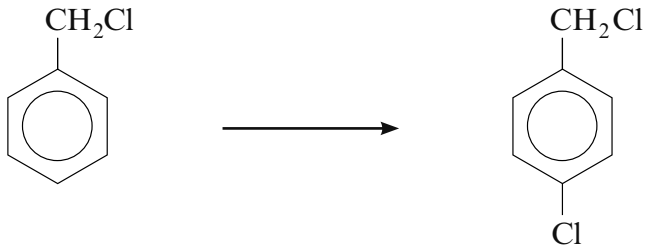
(b) Proline is a cyclic α-amino acid. In an aqueous solution of pH 6.3, proline exists largely as its zwitterion form.



(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]

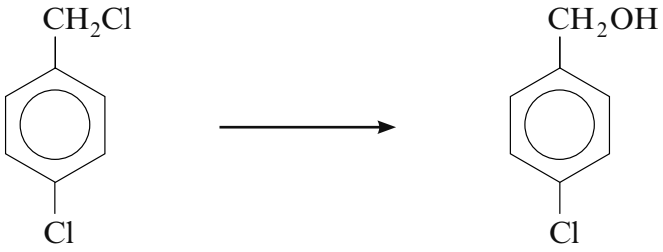
(c) (i) (Chloromethyl)benzene, $C_6H_5CH_2Cl$, reacts with chlorine in the presence of a catalyst to produce a mixture of isomers, **one** of which is 1-(chloromethyl)-4-chlorobenzene.



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.

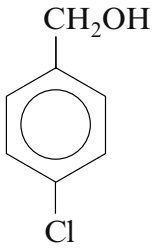


He wrote an outline of his method as follows.

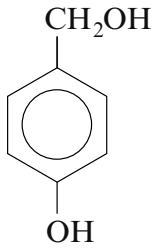
- Place 0.1 mol of the chloro-compound in a flask and add some sodium hydroxide solution of concentration 2 mol dm^{-3}.
- Reflux this mixture using an electrical heater.

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]

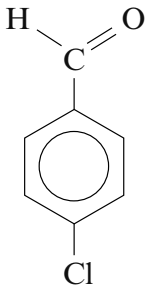


(4-chlorophenyl)methanol



(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

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 12 June 2013

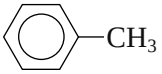
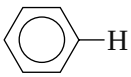
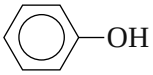
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

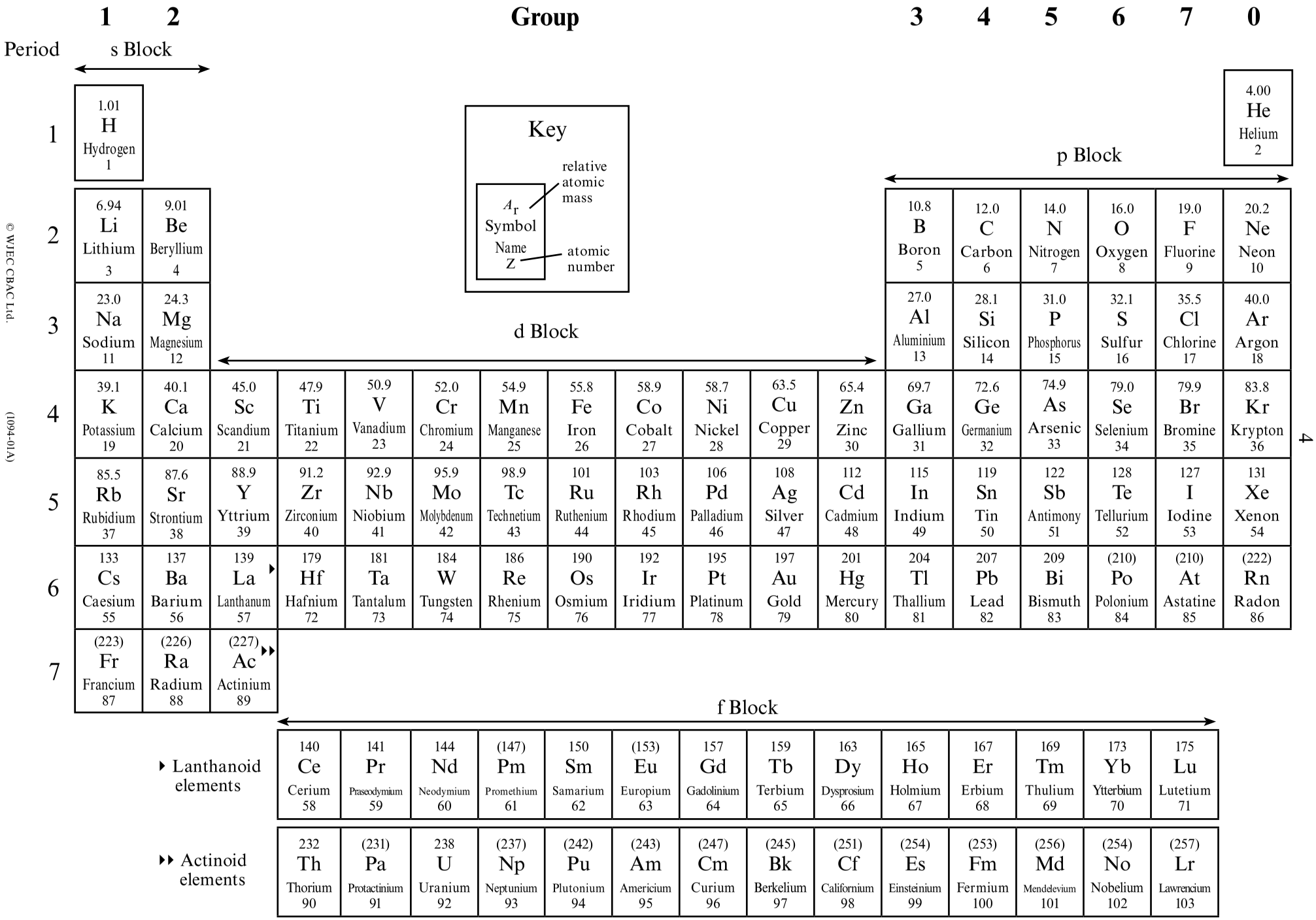
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
	2.2 to 2.3
$R-CH_2-$Halogen	3.3 to 4.3
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
	6.5 to 7.5
	7.0 *
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

SUMMER 2013

GCE CHEMISTRY – CH4

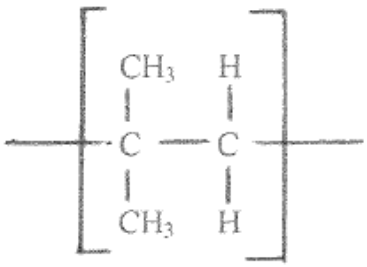
SUMMER 2013 MARK SCHEME

Q.1 (a) (i) (2-)Methylpropan-2-ol **[1]**

(ii) 30.1 / 30 **[1]**

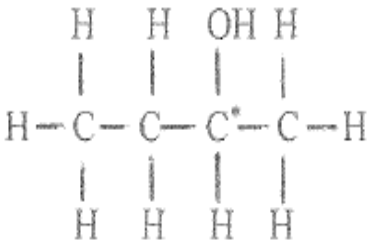
(iii) (Concentrated) sulfuric acid / phosphoric acid / aluminium oxide / pumice **[1]**

(iv)



(with or without n) **[1]**

(v)



(1) for structure, (1) for asterisk **[2]**

(vi) I acidified potassium dichromate / H^+, $Cr_2O_7^{2-}$(aq) **[1]**

II ethanal has a C = O bond at 1650-1750 cm^{-1}
(metaldehyde does not have this bond) (1)

metaldehyde has a C – O bond at 1000-1300 cm^{-1}
(ethanal does not have this bond) (1) **[2]**

(b) (i) **Reagent** 2,4-dinitrophenylhydrazine / 2,4-DNP OR iodine / NaOH or KI / NaOCl (1)

Observation yellow / orange / red precipitate OR yellow precipitate (1) **[2]**

(ii) **Reagent** ethanol / sulfuric acid OR $NaHCO_3$ OR Ag^+/NH_3 / Tollens' (1)

Observation sweet smelling liquid OR effervescence OR silver mirror (1) **[2]**

Total [13]

Q.2 (a) React with iron(III) chloride solution
Purple solution with phenol, no reaction with methyl propenoate

OR

React with aqueous bromine / bromine water
White precipitate with phenol (and bromine decolourised), bromine decolourised with methyl propenoate

(1) for reagent and (1) for observation with compound **[2]**

(b) (i) It absorbs all colours except yellow / absorbs the blue end of the spectrum and reflects yellow – do not accept 'emits' **[1]**

(ii) Tin / iron and concentrated hydrochloric acid **[1]**

(c) (i) Moles of 2,4-dinitrophenol = 7.36/184 = 0.040 (1)

Moles of 2,4-dinitrophenyl ethanoate = 7.91/226 = 0.035 (1)

Percentage yield = 0.035 × 100 / 0.040 = 87.5 /88 % (1) **[3]**

(ii) R_f value is given by $\frac{\text{distance travelled by the 2,4-dinitrophenol}}{\text{distance travelled by the solvent front}}$ (1)

$= \frac{2.8}{5.0} = 0.56$ (1) **[2]**

(d) (i) Nickel / platinum **[1]**

(ii) The –OH groups are able to hydrogen bond with water (1)
but these are a very small part of the 'urushiol' molecule (1) **[2]**

Total [12]

Q.3 (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)

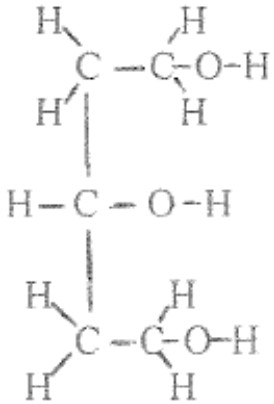
since M_r of water is 18 n = 1 (1) **[5]**

(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]

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

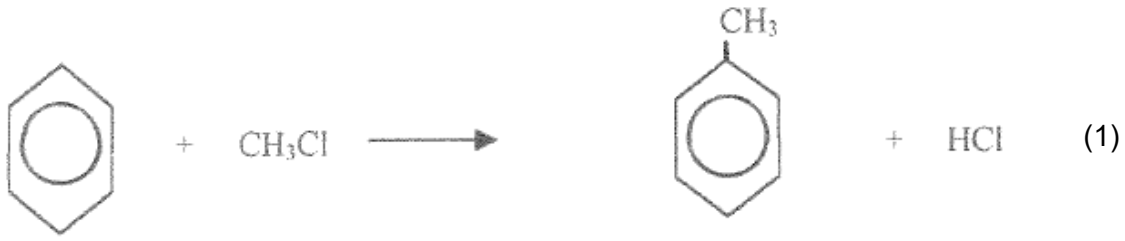
This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)
The π-cloud is **electron rich** and will be attracted to electron deficient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

[6]

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

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

(b)



(1)

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

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

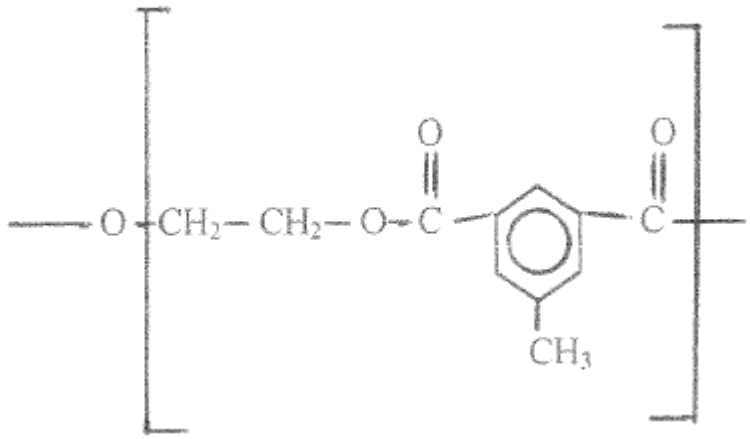
[3]

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

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

[4]

(iii)



[1]

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

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

[2]

Total [20]

Q.5 (a) (i) The **nitrogen atom** has a **lone pair** of electrons making it an electron pair donor / proton acceptor **[1]**

(ii) Compound **L** must contain the grouping  (1)

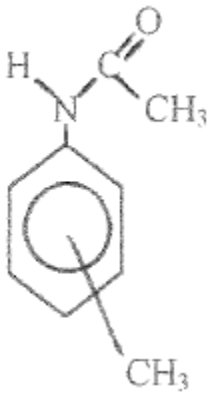
The nitrogen atom must be bonded directly to the ring as a (primary) aromatic amine is formed on hydrolysis (1)

As the hydrolysis compound is a phenol (and has an OH group directly bonded to the ring) a methyl group must also be bonded directly to the ring, as the molecular formula is C_7H_8O / the compound has the structure

 (1)

The compound is likely to be an amide, as these are hydrolysed by bases to amines (1)

A suggested formula is

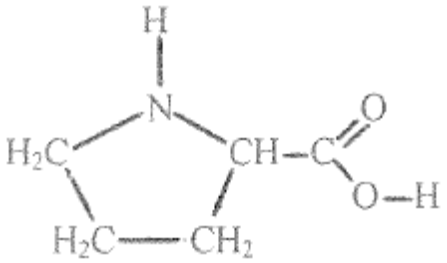
 (1)

which is $C_9H_{11}NO$,
an isomer of cathinone
/ has M_r of 149(1)

[6]

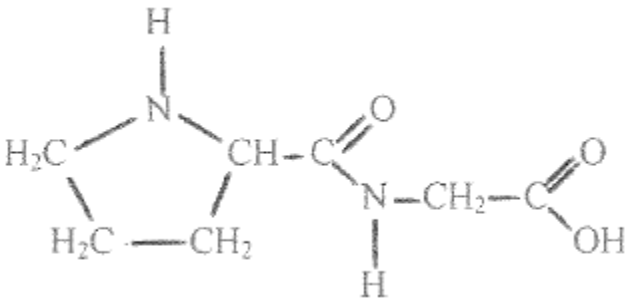
QWC Information organised clearly and coherently, using specialist vocabulary where appropriate *QWC* **[1]**

(b) (i)

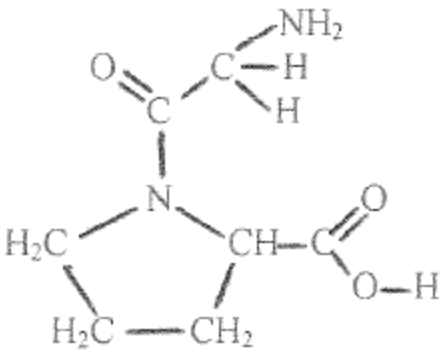


[1]

(ii)

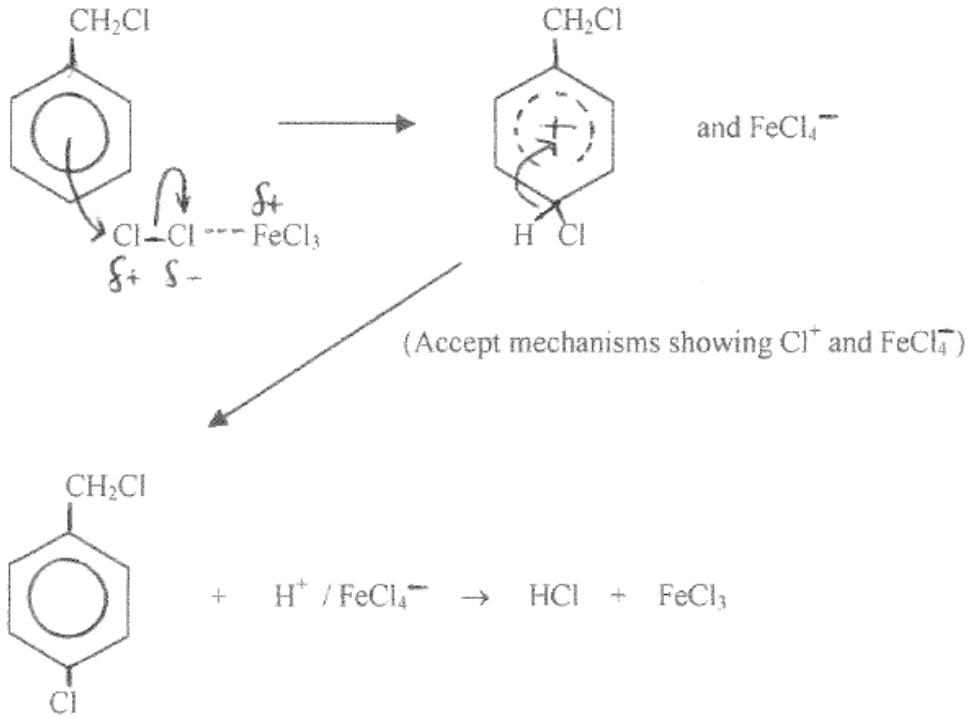


OR



[1]

(c) (i)



Correct catalyst (1)

Correct curly arrows and polarisation / formation of Cl^+ (1)

Wheland intermediate (1) Production of HCl and regeneration of $FeCl_3$ (1)

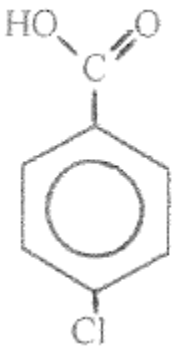
[4]

(ii) Volume of sodium hydroxide solution needed (1)
How long to reflux (1)

[2]

(iii) The aromatic C – Cl bond is stronger than the aliphatic C – Cl bond (1)
This is because a p-electron(s) of the chlorine atom in the aromatic compound becomes part of / incorporated into the delocalised π system of the ring (1) **[2]**

(iv)



(1)

chlorine has two isotopes 35/37 in a 3:1 ratio (1)

[2]

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

CHEMISTRY – CH4

P.M. MONDAY, 9 June 2014

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**12**	
	2.	**13**	
	3.	**15**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

Examiner only

SECTION A

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

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

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

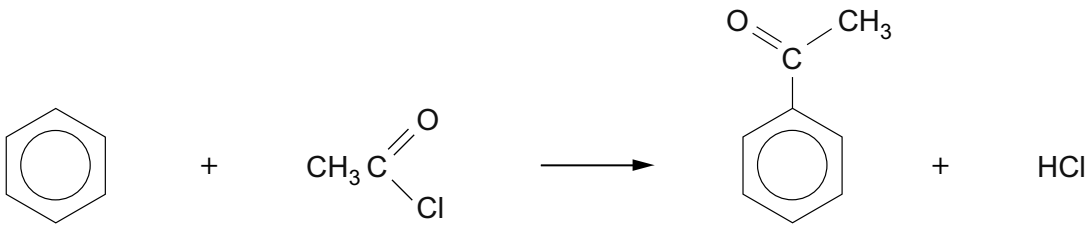
(ii) The free radical reaction of pentane with chlorine gives other chlorinated organic products. Give the structural formula of the carbon-containing free radical that leads to the formation of 2-chloropentane. [1]

.....

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

.....

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



phenylethanone

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

.....

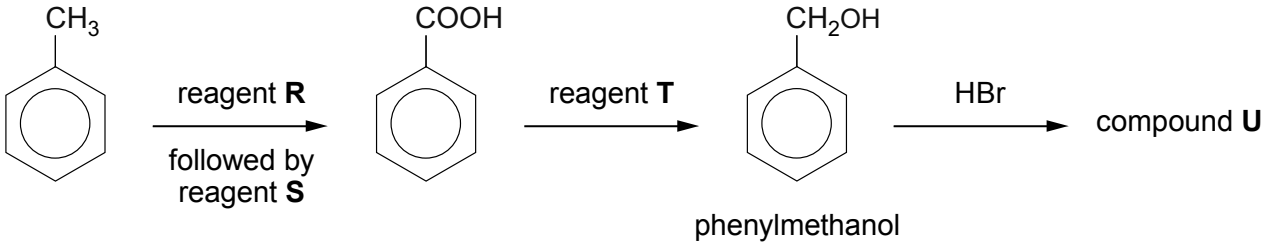
Examiner only

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

.....

.....

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



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

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

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

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

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

.....

.....

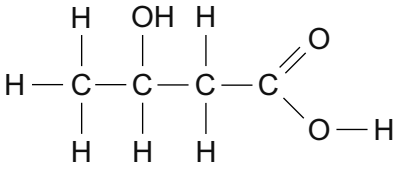
.....

Total [12]

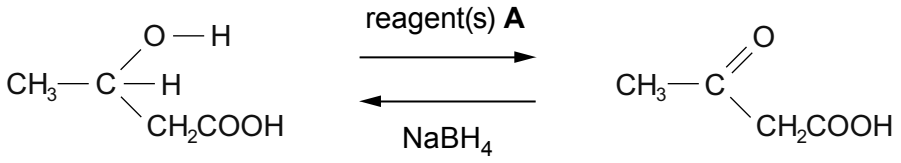
Examiner only

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

(a) Indicate the position of any chiral centre in the formula of 3-hydroxybutanoic acid by use of an asterisk (*). [1]



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



3-oxobutanoic acid

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

.....

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

I State what is meant by the term *racemic mixture*. [1]

.....

.....

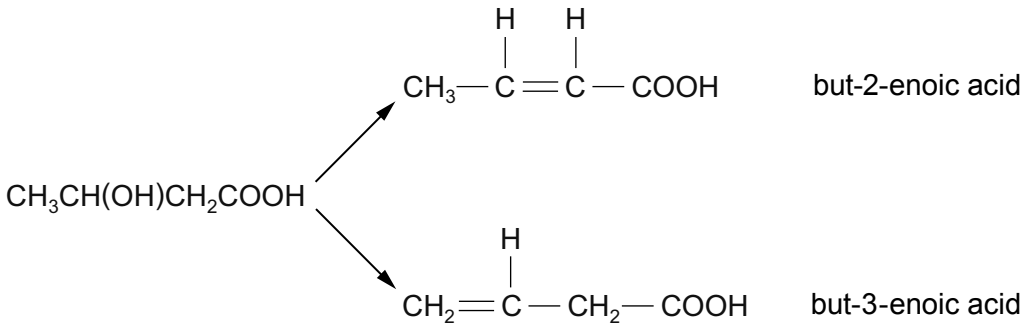
II State the effect (if any) that a racemic mixture has on the plane of polarised light. [1]

.....

.....

Examiner only

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



(i) State which of these unsaturated acids exists as *E*-*Z* isomers, giving a reason for your answer. [1]

.....

.....

.....

(ii) A scientist reported that the yield of the products was

but-2-enoic acid	89 %
but-3-enoic acid	4 %
together with unreacted 3-hydroxybutanoic acid	7 %

State any additional information that another scientist would have to know so that the experiment could be repeated to confirm these yields. [2]

1 .....

2 .....

(d) Both 3-hydroxybutanoic acid and 3-oxobutanoic acid will undergo the triiodomethane (iodoform) reaction. State the reagent(s) used for this reaction and the observation made. [2]

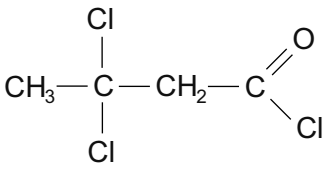
Reagent(s) .....

Observation .....

1094 010005

Examiner only

(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]

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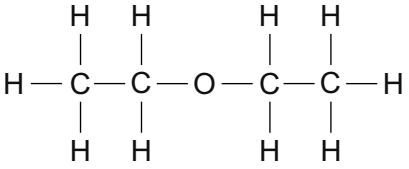
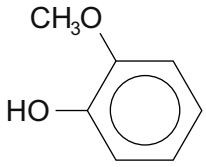
3. *Read the passage below and then answer the questions in the spaces provided.*

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

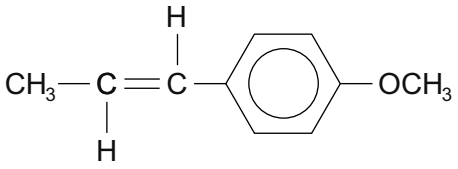
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



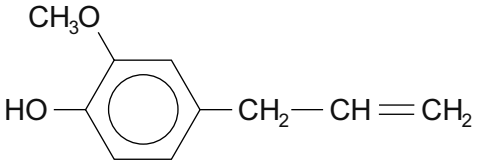
ethoxyethane



guaiacol

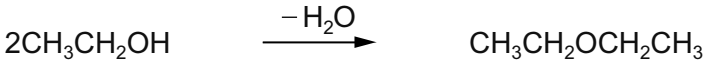


anethole

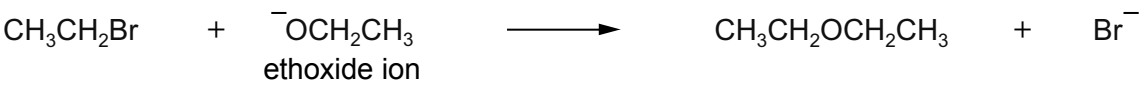


eugenol

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



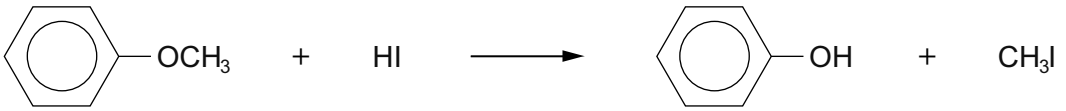
Another method is by reacting bromoethane with sodium ethoxide (a source of the ethoxide ion).



ethoxide ion

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

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



methoxybenzene

Examiner only

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

- End of passage -

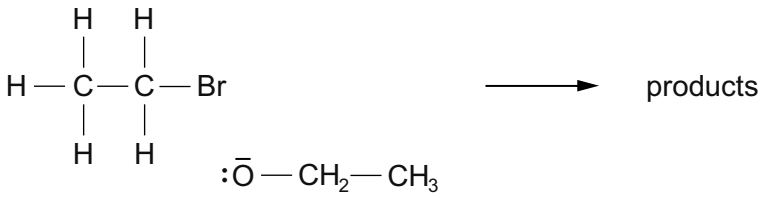
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol (M_r = 46) and obtained a 45 % yield of ethoxyethane (M_r = 74). Calculate the mass of ethoxyethane obtained. [3]

Mass = ... g

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

.....

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



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

.....

.....

Examiner only

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

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

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

.....

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

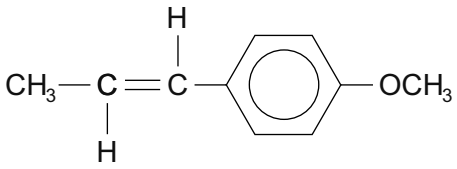
Reagent .....

Observation .....

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

.....

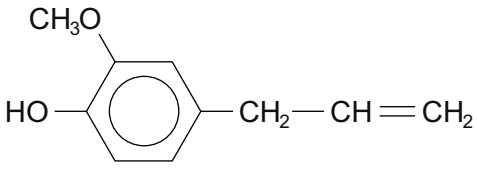
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



anethole

displayed formula of product

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



eugenol

displayed formula for compound **Y**

Functional group .....

Total [15]

Total Section A [40]

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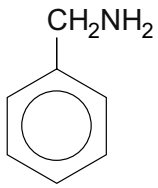
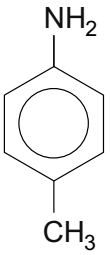
SECTION B

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

4. *(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]

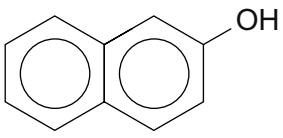
(ii) State and explain how the mass spectra of these two compounds would differ. [1]

(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.

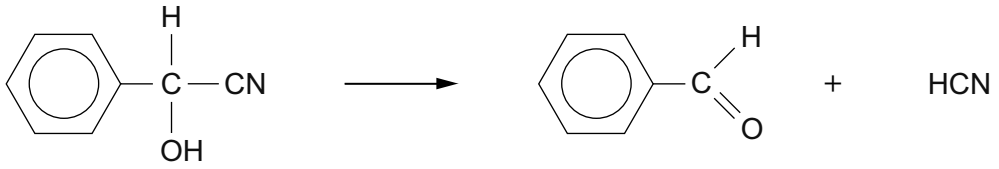


naphthalene-2-ol

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]

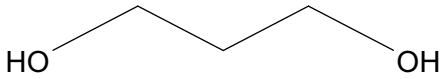
TURN OVER FOR QUESTION 5

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.

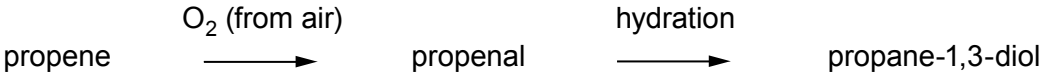
- It contains C, 71.3 % and H, 9.6 % by mass. The remainder is oxygen.
- Only one oxygen atom is present in each molecule.
- It gives a silver mirror with Tollens' reagent (ammoniacal silver nitrate solution).
- The mass spectrum shows a fragmentation ion, containing only carbon and hydrogen, at m/z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



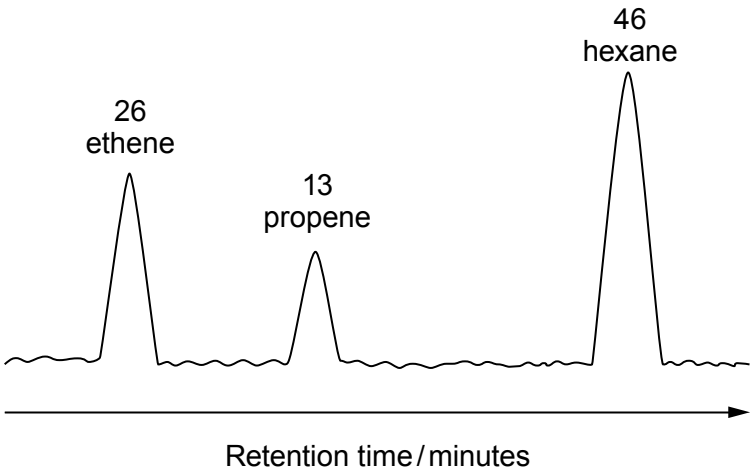
One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.



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

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. MONDAY, 9 June 2014

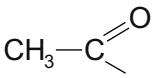
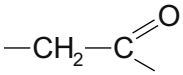
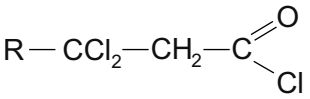
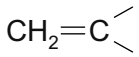
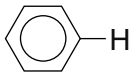
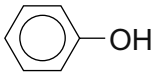
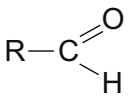
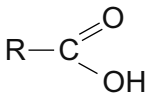
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

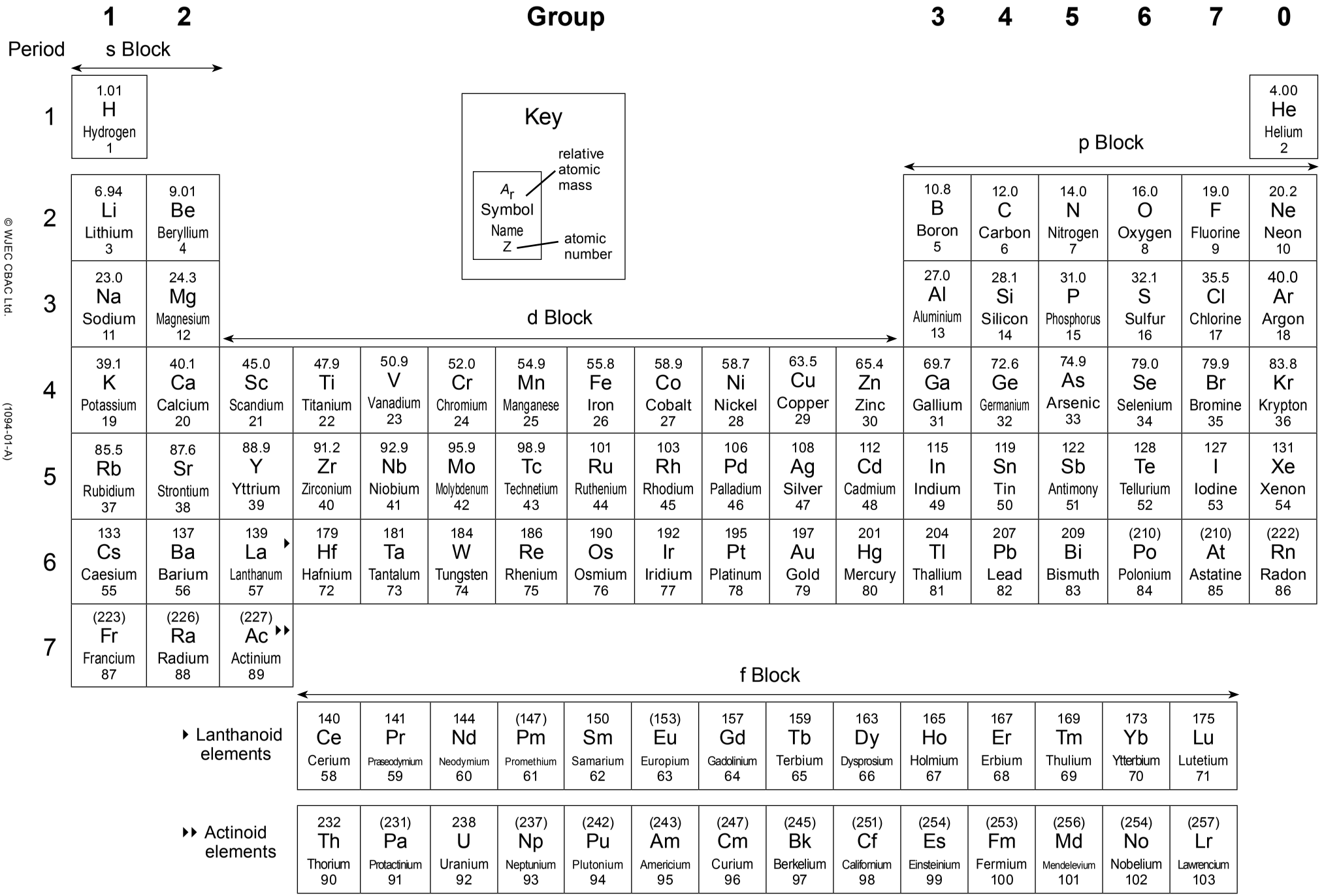
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
CH_3-CCl_2-	2.0 to 2.5
	2.0 to 3.0
	2.5 to 3.0
$R-CH_2-Cl$	3.3 to 4.3
$R-OH$	4.5 *
	4.8
	6.5 to 7.5
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

SUMMER 2014

GCE CHEMISTRY – CH4

SUMMER 2014 MARK SCHEME

SECTION A

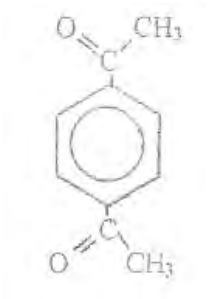
Q.1 (a) (i) $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2CH_2CH_2Cl + HCl$ [1]

(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

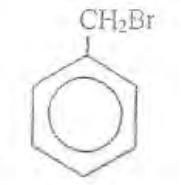
It must contain a C=O group but it is not an aldehyde as it does not react with Tollens' reagent (1) [2]

(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)

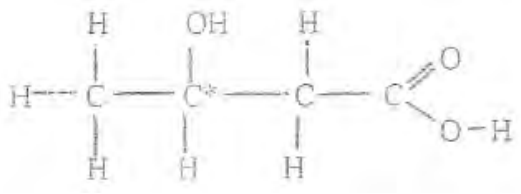


[1]

(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]

Q.2 (a)



[1]

(b) (i) Acidified potassium dichromate allow H^+, $Cr_2O_7^{2-}$ [1]

(ii) I An equimolar mixture of two enantiomers / optical isomers
do not accept 'equal mixture' [1]

II It has no (apparent) effect on the plane of polarised light [1]

(c) (i) But-2-enoic acid; this is because each of the carbon atoms of the double bond has two different groups / atoms
allow reason based on the other isomer [1]

(ii) Any TWO from the following for (1) each
reagent used / temperature / quantities / time of reaction / catalyst / solvent [2]

(d) Reagent(s) KOH / I_2 or NaOCl / KI (1) allow names
Observation Yellow precipitate (1) [2]

(e) The NMR spectrum will consist of two peaks, as there are two discrete 'areas' of protons; these will be seen at between 2.0 to 2.5 (CH_3) and between 2.5 to 3.0 (CH_2) (1)
The peak area ratio will be 3:2 for the CH_3 and CH_2 protons respectively (1)
There will be no splitting of either signal as the protons causing these signals are not bonded directly to other carbon atoms that also have protons (1)

1 max if only one peak described correctly [3]

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

Total [13]

Q.3 (a) (i) 2 mol of ethanol gives 1 mol of ethoxyethane (1)

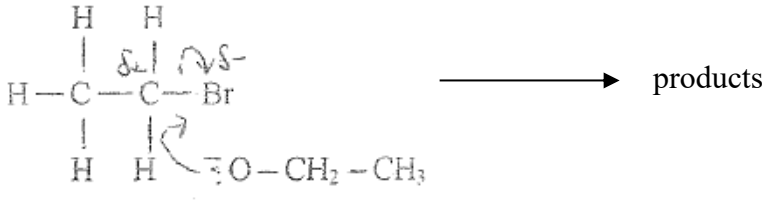
Moles of ethanol = $\frac{69}{46}$ = 1.5

∴ 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]

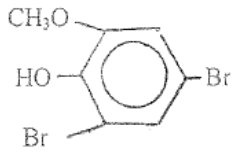
(iii)



(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

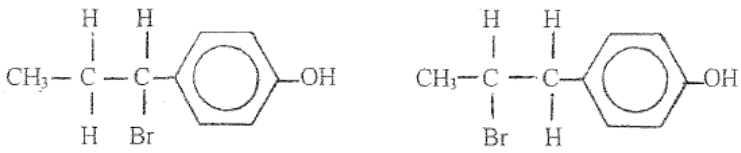
(ii) Bromine decolorised / orange to colourless / white solid [1]

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

Observation Purple coloration / solution (1) [2]

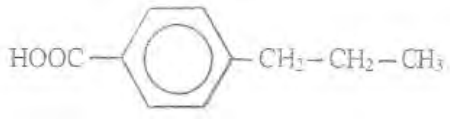
(d) (i) $C_{10}H_{12}O_1$ [1]

(ii)



[1]

(e) Displayed formula, for example



(1)

Functional group carboxylic acid (1) [2]

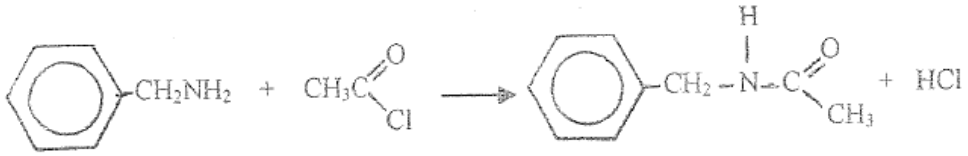
Total [15]

SECTION B

Q.4 (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]

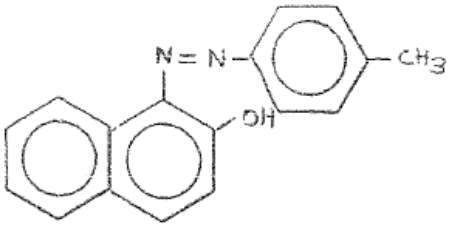
II Heated electrically / by a naked flame with a water bath (1)
Add compound **G** to the ethanol until the hot ethanol will (just) not dissolve any more solute (1)
Filter hot (1)
Allow to cool (1)
Filter (1)
Dry in air / window sill / < 60 °C in an oven (1) [5]

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]

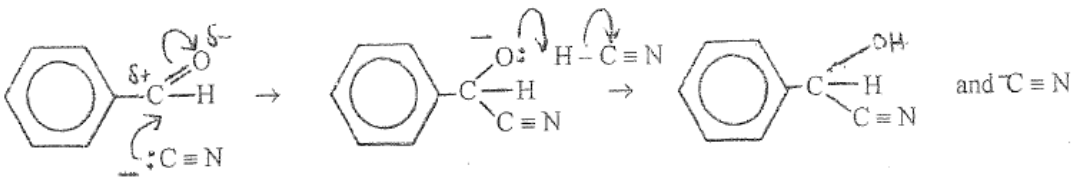
(iv) I The amine is reacted with sodium nitrite / HCl(aq) or nitrous acid (1) at a temperature of < 10 °C (1) [2]

II



[1]

(b) (i) Nucleophilic addition (1)

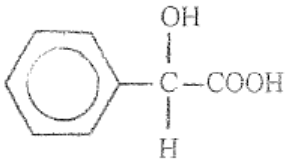


Accept a mechanism that shows HCN polarisation and nucleophilic addition as a concerted process

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]

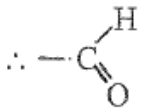
Q.5 (a) C 71.3 H 9.6 ∴ O 19.1 (1)

÷ by A_r $\frac{71.3}{12} = 5.94$ $\frac{9.6}{1.0} = 9.6$ $\frac{19.1}{16} = 1.193$

÷ smallest $\frac{5.94}{1.193} = 5$ $\frac{9.6}{1.193} = 8$ $\frac{1.193}{1.193} = 1$ (1)

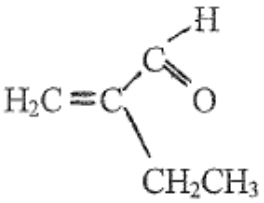
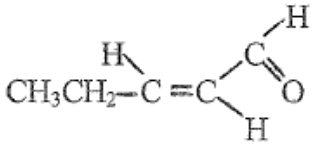
Only one oxygen atom per molecule

∴ Molecular formula is C_5H_8O (1)

Silver mirror produced ∴  present (1)

Ion m/z 29 suggests ethyl group present / CH_3CH_2 (1)

Structure must be

 or  (1)

[6]

(b) (i) $C_{11}H_{24} \longrightarrow C_6H_{14} + C_2H_4 + C_3H_6$ [1]

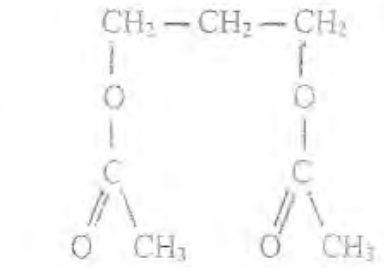
(ii) Total peak areas 26 + 13 + 46 = 85

% propene = $\frac{13 \times 100}{85}$ = 15.(3) [1]

(iii) Any THREE points for (1) each [3]

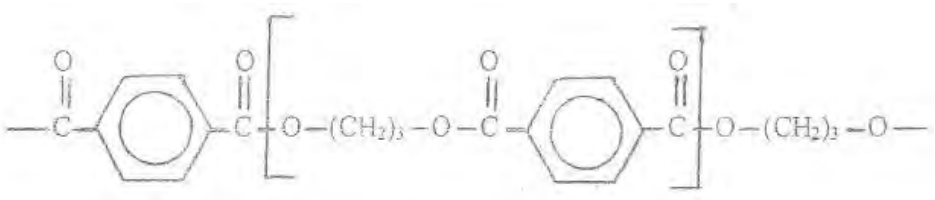
e.g. can it run at a lower temperature (reducing energy costs)
is the yield comparable / better than the yield from the propene process
is the time taken comparable / better than used in the propene process
is there a continued availability of starting materials
can the product be easily / better separated from the reaction mixture
is relatively more expensive equipment needed
is it a batch or continuous process

(iv)



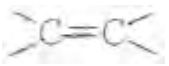
[1]

(c) (i)



[1]

(ii) The production of PTT is an example of condensation polymerisation (1)
The production of poly(propene) is an example of addition polymerisation (1)
Condensation polymerisation needs bifunctional compounds / COOH,OH etc (1)

Addition polymerisation needs a  present in the monomer (1)

Addition polymerisation has an atom economy of 100% (1)
Condensation polymerisation has an atom economy of < 100%
(as a co-product is formed) (1) [6]

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

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1094/01

S15-1094-01

CHEMISTRY – CH4

P.M. WEDNESDAY, 10 June 2015

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**12**	
	2.	**12**	
	3.	**16**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1094 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

Examiner only

SECTION A

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

1. *(a)* Complete the gaps in the following sentences choosing from the words: [3]

blue **yellow** **higher** **lower**

Each word can be used once, more than once or not at all.

Benzene is a colourless compound that absorbs energy in the ultraviolet region of the electromagnetic spectrum.

Nitrobenzene is a yellow compound that absorbs energy in the ..... region of the visible spectrum.

The absorption of energy for benzene occurs at a ..... energy and at a ..... frequency than for nitrobenzene.

(b) Methylbenzene can be produced from benzene using a Friedel-Crafts reaction.

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

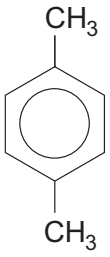
(ii) State the role of the catalyst used in this reaction, apart from increasing the rate. [1]

.....

.....

Examiner only

(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.



The low resolution proton NMR spectrum of this compound shows two peaks with a peak area ratio of 3:2.

Explain how 1,4-dimethylbenzene produces this spectrum. [2]

.....

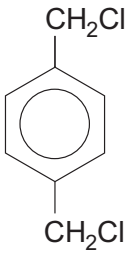
.....

.....

.....

1094 010003

(d) 1,4-Dimethylbenzene reacts with chlorine in a free radical reaction to give the liquid 1,4-di(chloromethyl)benzene.



(i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

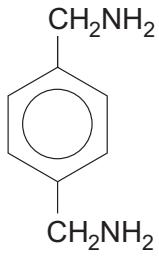
Method 1 .....

Method 2 .....

(ii) Give the displayed formula of the compound produced when 1,4-di(chloromethyl)benzene reacts with an excess of aqueous sodium hydroxide. [1]

Examiner only

(e) (i) 1,4-Di(chloromethyl)benzene reacts with ammonia to give the diamine below.



Draw the repeating section of the polymer obtained when this diamine reacts with benzene-1,4-dicarboxylic acid. [1]

(ii) The polymer obtained in *(e)*(i) above contains a peptide linkage.

State the name of a naturally occurring material that also contains a peptide linkage. [1]

.....

Total [12]

12

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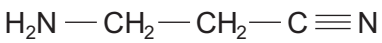
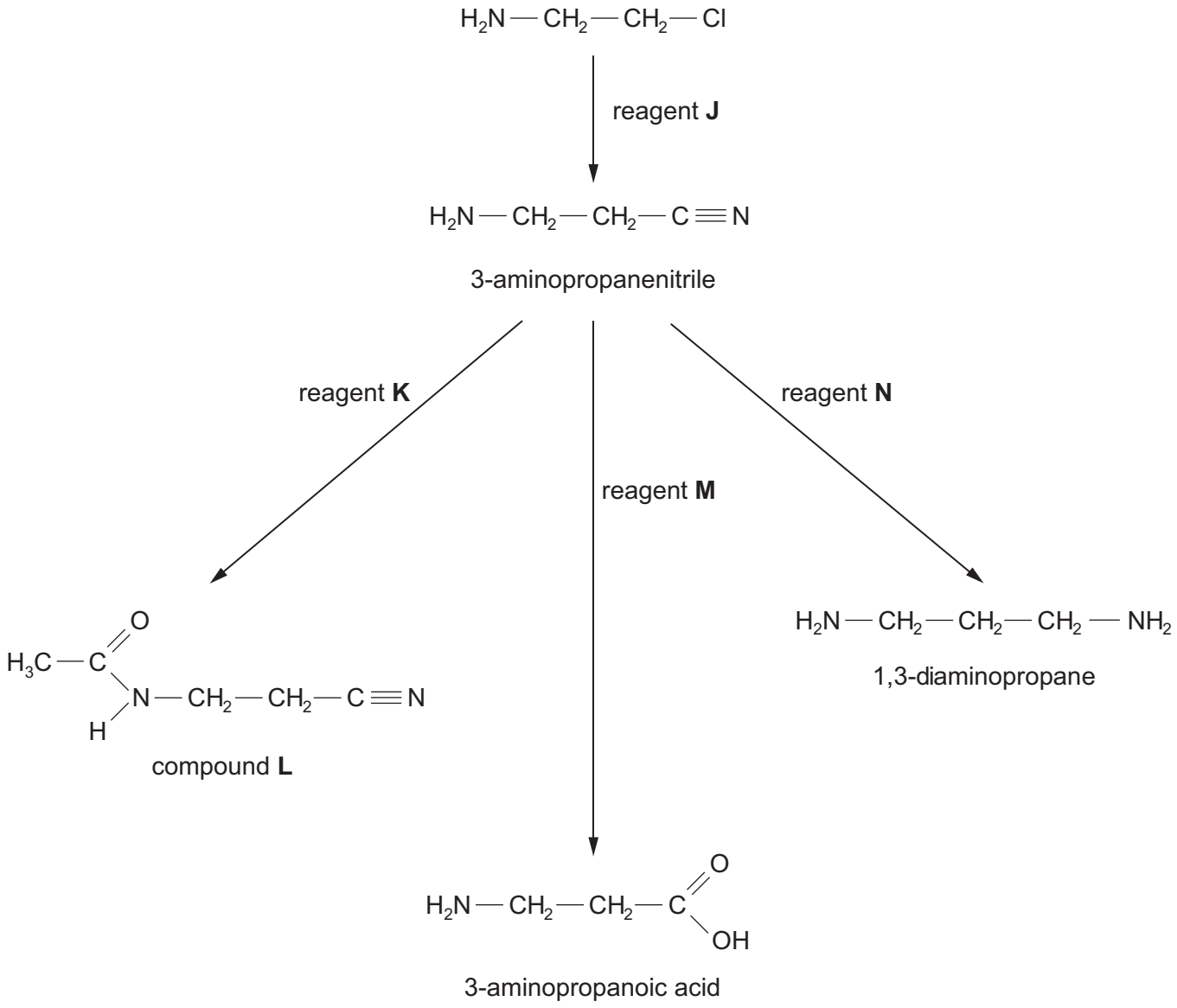
2. *(a)* Seeds of the sweet pea plant contain 3-aminopropanenitrile.



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



Examiner only

(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 α-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]

.....

.....

Examiner only

(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]

12

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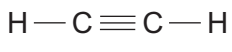
3. *Read the passage below and then answer the questions in the spaces provided.*

Some chemistry of the alkynes

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

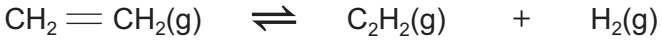
The simplest member of the series is ethyne (acetylene). All alkynes contain a carbon to carbon triple bond (C≡C).



ethyne

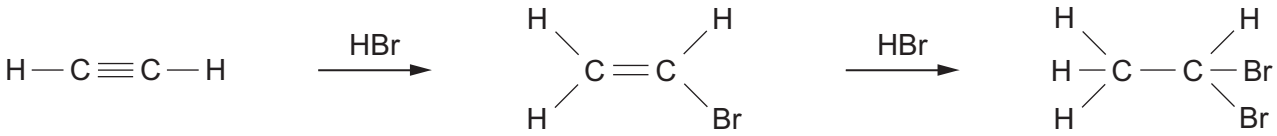
Until 50 years ago ethyne was the main starting material for the preparation of aliphatic compounds. It was made by the reaction of calcium carbide with water.

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.

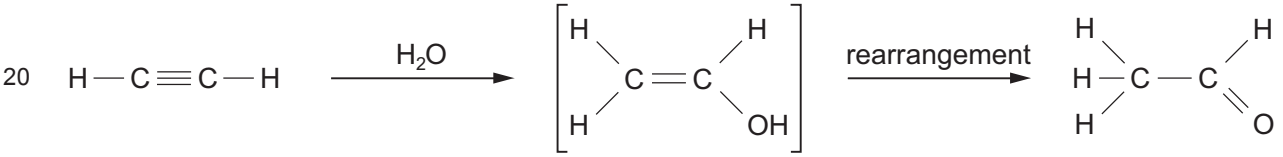


One laboratory method for making ethyne is by reacting 1,2-dibromoethane with an excess of alcoholic potassium hydroxide solution. Potassium bromide and water are the other products of this reaction.

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



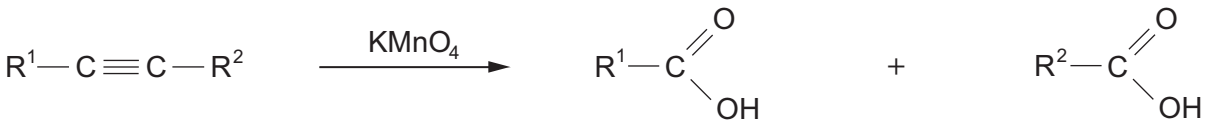
When ethyne is passed into aqueous sulfuric acid, containing mercury(II) ions as a catalyst, ethanal is produced.



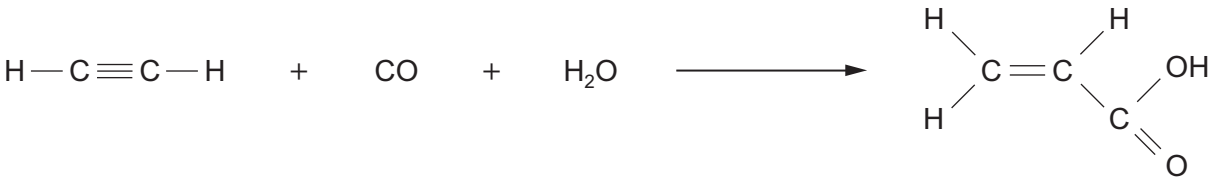
ethenol

Examiner only

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.



- 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]

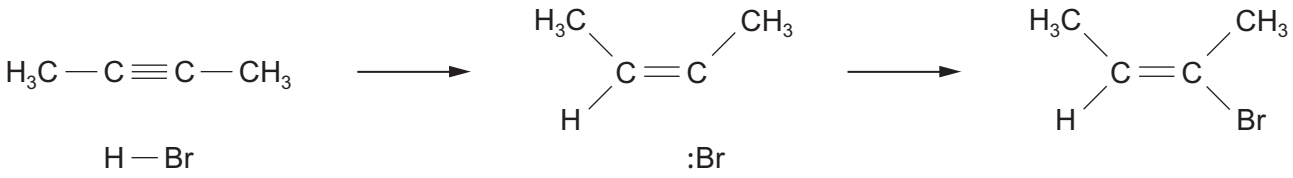
.....

.....

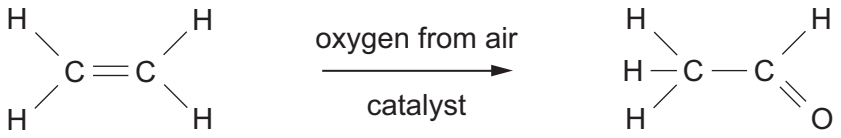
Examiner only

(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]

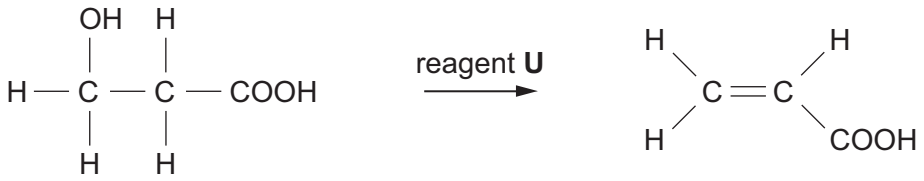
Displayed formula *Empirical formula* .....

Examiner only

(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]

16

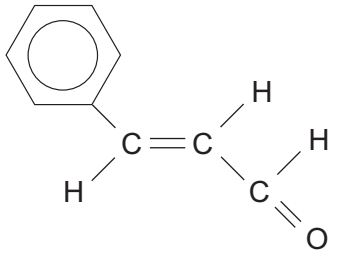
Total Section A [40]

Turn over.

SECTION B

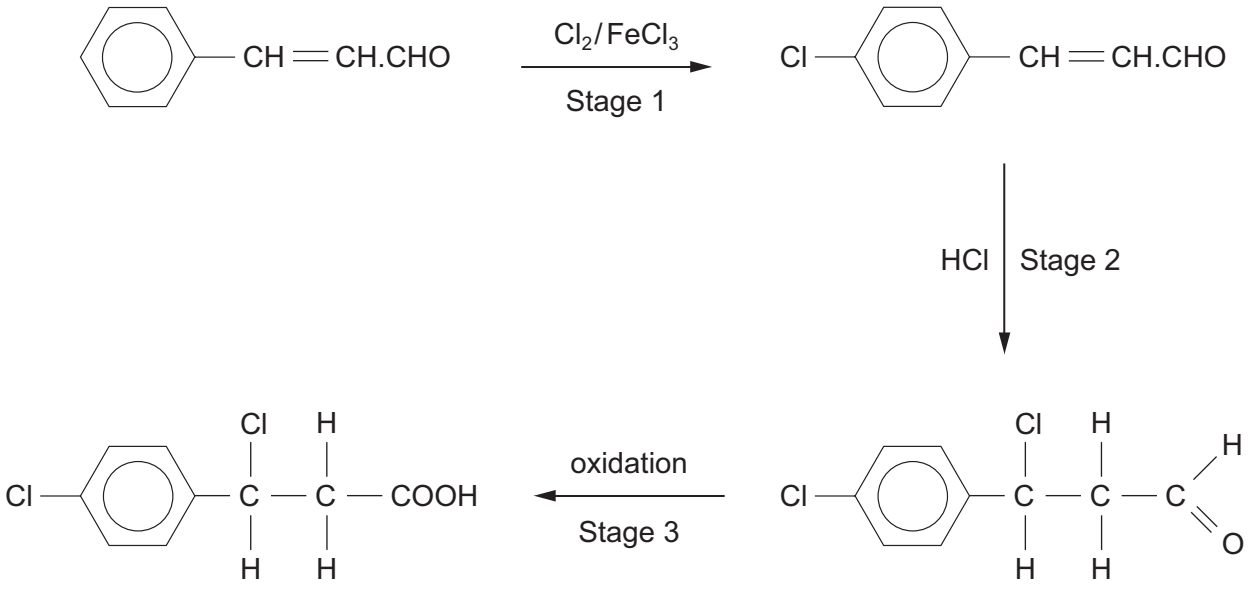
Answer **both** *questions in the separate answer book provided.*

4. *(a)* Cinnamaldehyde (3-phenylprop-2-enal) is a pale yellow liquid that occurs in the oil obtained from the bark of cinnamon trees.



cinnamaldehyde

An organic chemist suggested the following method for producing compound **M** from cinnamaldehyde.



compound **M**

(i) Suggest **two** reasons why the reaction of cinnamaldehyde with chlorine is **unlikely** to give only the compound shown and give the displayed formula of another possible product. [3]

(ii) Give the displayed formula of another product that may be formed when hydrogen chloride is added across the double bond in the second stage, explaining why this can occur. [2]

(iii) State the name of a suitable oxidising agent for stage 3. [1]

(iv) Explain why compound **M**, made in this way from cinnamaldehyde, has no effect on the plane of polarised light. [2]

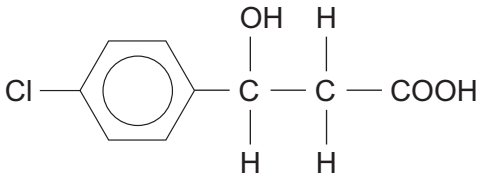
QWC [1]

(v) Bethan attempted to reverse stage 3 by using a reducing agent. Suggest a suitable reducing agent that she should use and give the displayed formula of a different product that could be an impurity in her product. [2]

(b) You are given a pure sample of compound **M** and asked to carry out some reactions with it.

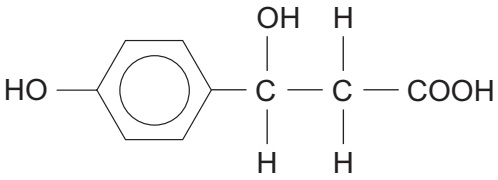
(i) A sample is added to aqueous sodium hydrogencarbonate. State what is seen during this reaction and name the functional group that has been confirmed. [2]

(ii) Compound **M** is heated under reflux with aqueous sodium hydroxide, followed by acidification. The organic product of this reaction is compound **N**.



compound **N**

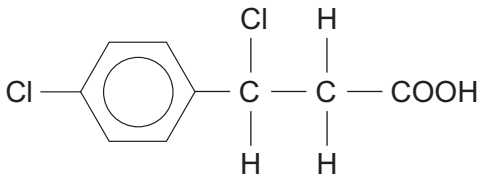
Explain why compound **N** is formed in preference to compound **P**.



compound **P**

[2]

(c) Compound **R** is an isomer of compound **M** (whose formula is shown below).

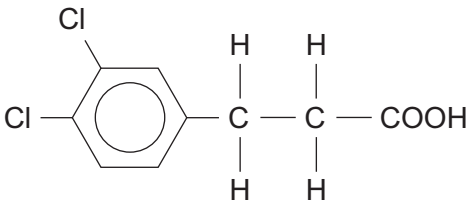


compound **M**

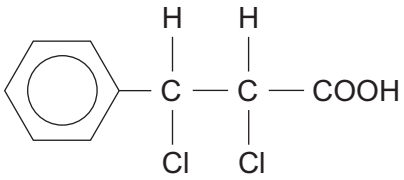
Tests on compound **R** show that it:

- does not contain a chiral centre;
- has an aromatic-containing fragment at m/z 77 in its mass spectrum;
- is not quickly hydrolysed by the addition of water.

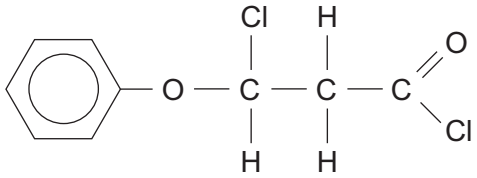
Three compounds that do **not** fit this information are shown below.



compound **1**



compound **2**



compound **3**

Discuss why **each** of these structures is **not** the formula for compound **R**, giving **one** reason for **each** compound. Give the displayed formula of a compound of your choice that **does fit** the information given for compound **R**. [4]

QWC [1]

Total [20]

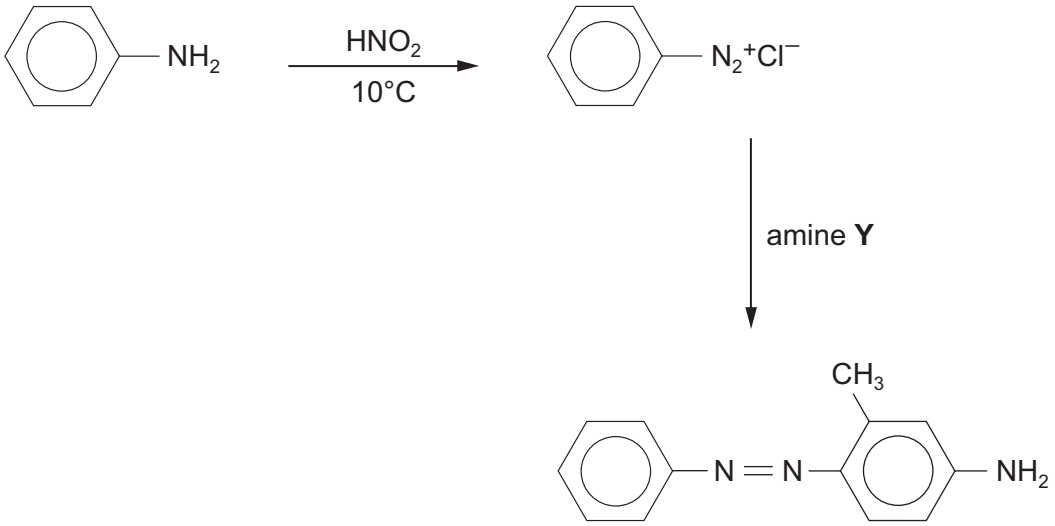
5. *(a)* Primary aliphatic amines react with nitric(III) (nitrous) acid to give a quantitative yield of nitrogen gas, and an alcohol as the major organic product.

In an experiment 2.54 g of an amine gave 1.00 dm^3 of nitrogen, measured at 10 °C.

Calculate the relative molecular mass of the amine and hence its structural formula.

[At 10 °C, 1 mol of nitrogen gas has a volume of 23.2 dm^3] [3]

(b) At 10 °C and below a primary aromatic amine reacts with nitric(III) acid, HNO_2, to give a diazonium compound, which can then be coupled with a phenol or an amine.
An example of this reaction is shown below.

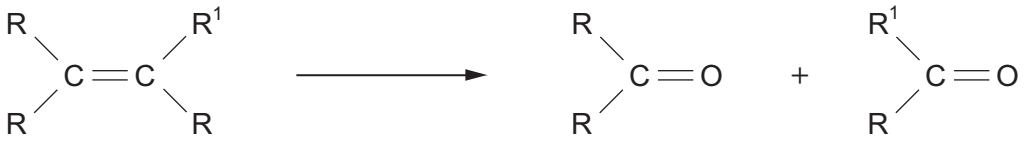


(i) The benzenediazonium ion acts as an electrophile in this reaction.
State the meaning of the term electrophile. [1]

(ii) State the **name** of amine **Y**. [1]

(iii) The product of this reaction contains an — N = N — group bonded to aromatic systems. State the general name for this type of grouping, which can give coloured compounds, and state why this type of reaction has industrial importance. [2]

(c) Alkenes react with ozone to give an intermediate product that can then be reduced to give aldehydes or ketones.



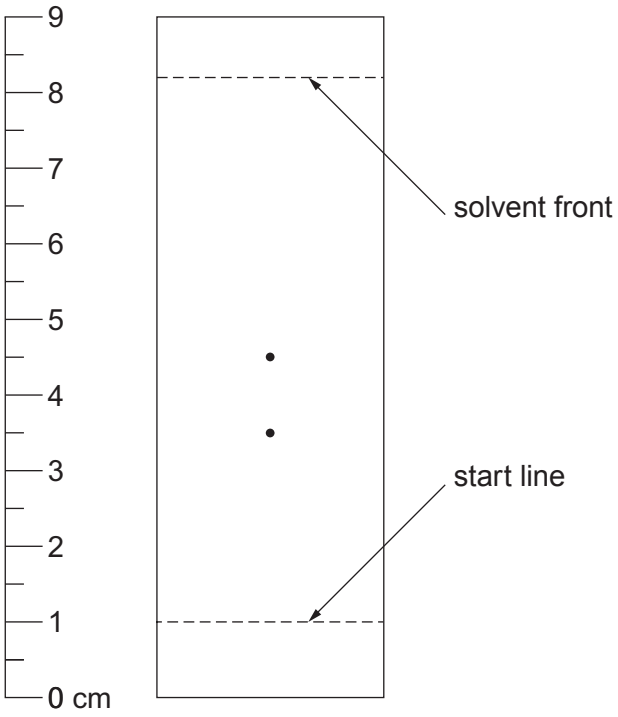
alkene **W**

An alkene **W** was reacted in this way to give two different ketones. R and R^1 represent **two different** alkyl groups.

These ketones were then separated by thin layer chromatography to give two spots. The ketone spots were colourless and their presence was found by spraying the chromatogram with a solution of 2,4-dinitrophenylhydrazine.

(i) State the type of reaction that occurs when a ketone reacts with 2,4-dinitrophenylhydrazine and how this reaction is able to show the presence of these ketones in the chromatogram. [2]

(ii) The chromatogram that was obtained is shown below.
Use the table of R_f values to identify the two ketones present and hence the displayed formula and the name of alkene **W**. [4]
QWC [1]



Ketone	R_f value
propanone	0.35
butanone	0.40
pentan-2-one	0.49
pentan-3-one	0.60
hexan-2-one	0.68

(iii) State how the **equation** for the reaction of alkene **W** with ozone shows that **W cannot be** 2-methyl-3-ethylpent-2-ene, $(CH_3)_2C{=}C(CH_2CH_3)_2$. [1]

(d) This is a brief method written by a student to enable others to prepare ethyl ethanoate by esterification.

- Heat under reflux together 0.45 mol of ethanoic acid with an equimolar quantity of ethanol
- Add 5 cm^3 of sulfuric acid
- Distil off everything boiling up to 82 °C
- Add the distillate to aqueous sodium hydrogencarbonate in a separating funnel
- Run off the ethyl ethanoate layer and dry it over anhydrous calcium chloride
- Distil off the dried ethyl ethanoate and collect the fraction boiling at 75-78 °C

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

(ii) Calculate the mass of ethanoic acid needed for this experiment. [1]

(iii) State an important detail that is missing from the first bullet point. [1]

(iv) State why the sulfuric acid should have been added at the refluxing stage. [1]

(v) State why sodium hydrogencarbonate needed to be added to the distillate. [1]

Total [20]

Total Section B [40]

END OF PAPER

GCE A level

1094/01-A

S15-1094-01A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 10 June 2015

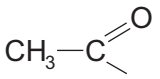
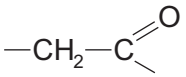
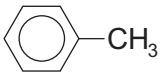
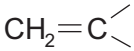
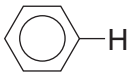
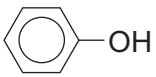
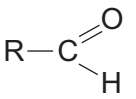
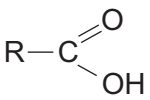
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

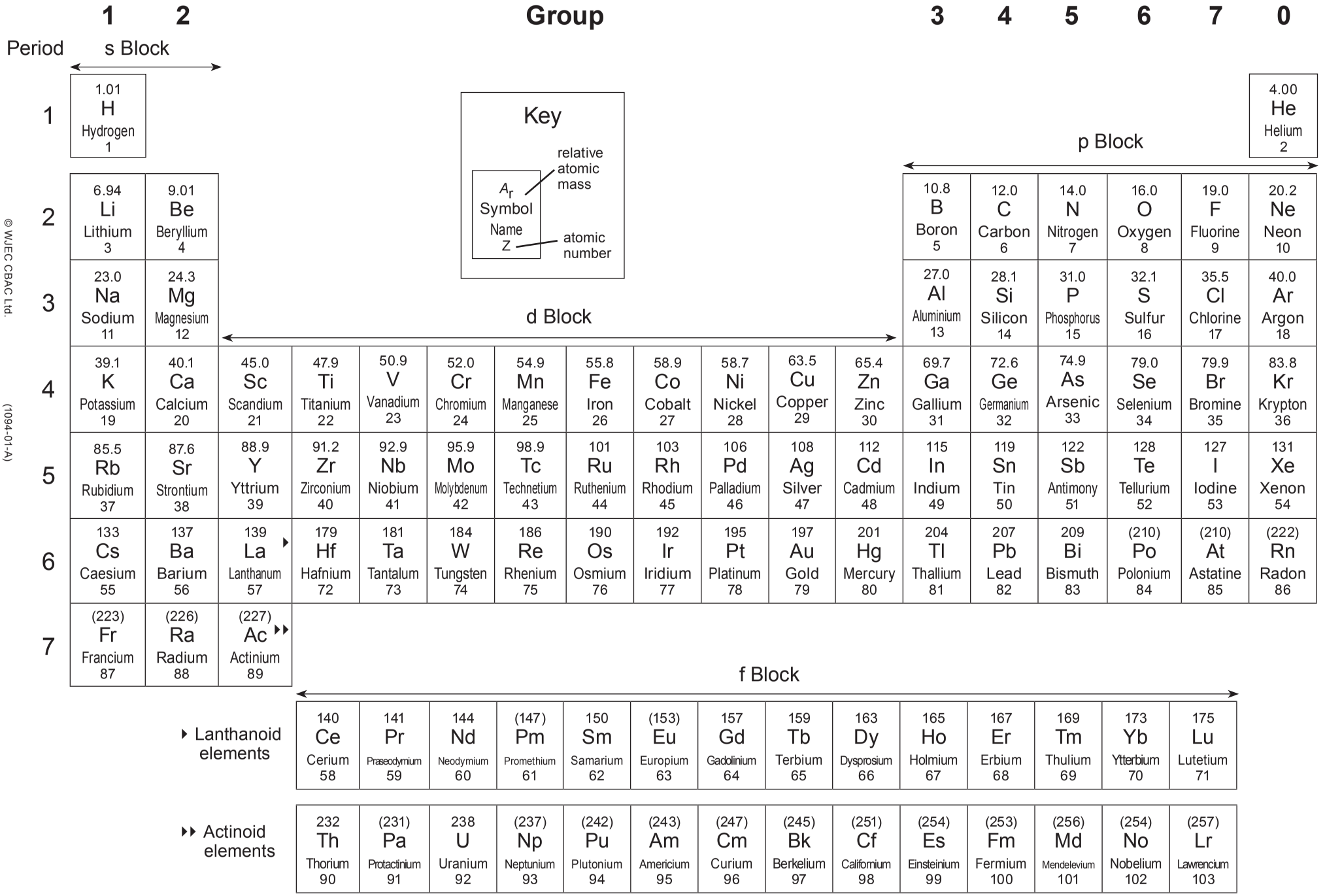
Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
$R-CH_2-$Halogen	3.3 to 4.3
$-O-CH_3$, $-OCH_2-R$, 	3.5 to 4.0
$R-OH$	4.5 *
	4.8
	6.5 to 7.5
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

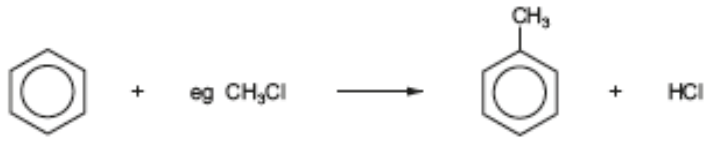


CH4

SECTION A

1. (a) ……blue …….. (1) ……higher (1) ……higher (1) [3]

(b) (i)



[1]

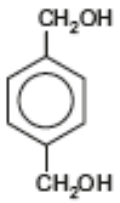
accept C_6H_5 in place of the ring accept equations that show the catalyst

(ii) It acts as a halogen carrier / it helps produce the electrophile/CH_3^+ / increases polarity of the halogenoalkane [1]

(c) There are 6 methyl protons and 4 aromatic protons, hence a ratio of 3:2 (1)
All the methyl protons are equivalent as are all the aromatic protons (1) [2]

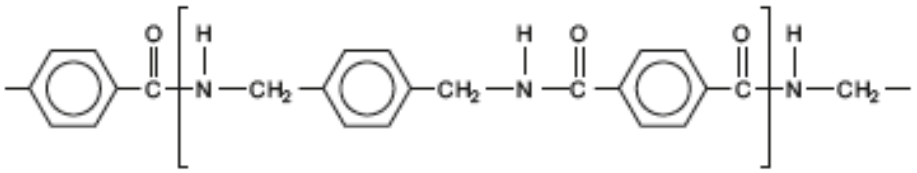
(d) (i) Any 2 from NMR / HPLC / GC / refractive index / mass spectra / boiling temperature [2]

(ii)



[1]

(e) (i)

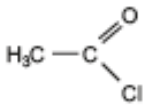


[1]

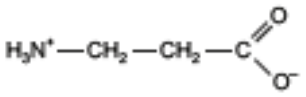
(ii) protein / dipeptide / polypeptide [1]

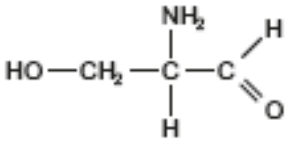
Total [12]

2. (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]

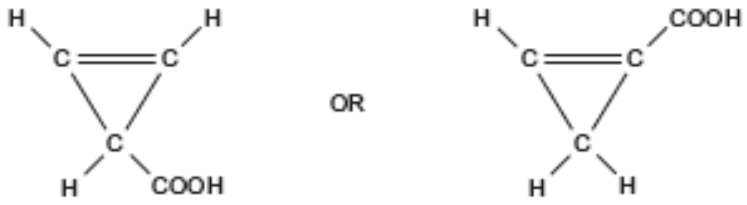
(b) (i) Molecular formula is $C_4H_4O_2$ [1]

(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]

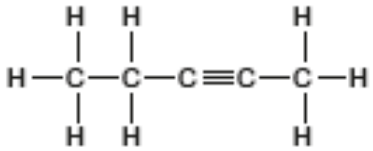
(v) Possibilities



[1]

Total [12]

3. (a)



[1]

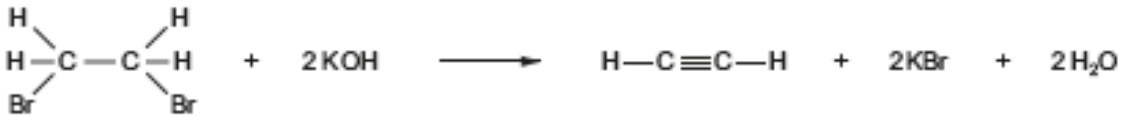
(b) Moles of calcium carbide = 500/64.1 = 7.80 (1)

Moles of ethyne = 7.80

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

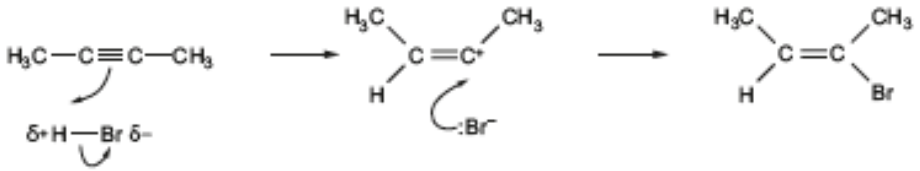
(c) If the process is endothermic left to right then it needs to absorb energy
– hence the high temperature / endothermic reactions need a high temperature [1]

(d)



[1]

(e)

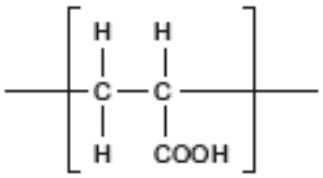


Curly arrows (1), full (1) and partial charges (1) [3]

(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]

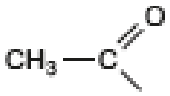
(h) (i)



[1]

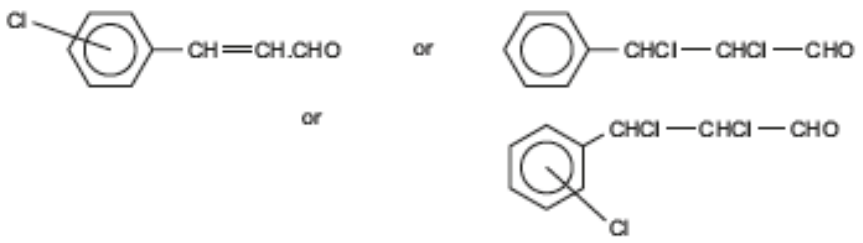
(ii) I sulfuric acid / H_2SO_4 / phosphoric acid / H_3PO_4 / Al_2O_3 [1]

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]

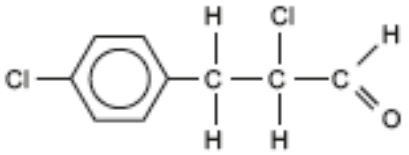
4. (a) (i) Substitution may occur in the ring at a different position (1)
Addition may occur across the double bond (1)



(1)

[3]

(ii)



(1)

In both additions a secondary carbocation is formed therefore 'equal chances' /
the energy for the formation of the carbocation is similar in both cases (1)

[2]

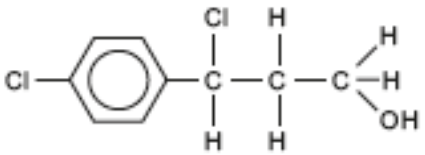
(iii) 'acidified dichromate' / H^+ and $Cr_2O_7^{2-}$ [1]

(iv) Although it contains a chiral centre (1) an equimolar / racemic mixture has been produced in the reaction (1) rotation is (externally) compensated (1)

Any 2 from 3 [2]

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

(v) $LiAlH_4$ / lithium tetrahydridoaluminate(III) / lithium aluminium hydride (1)
Do not accept $NaBH_4$



(1)

[2]

(b) (i) Gas bubbles / effervescence (1) Identifies carboxylic acid group (1) [2]

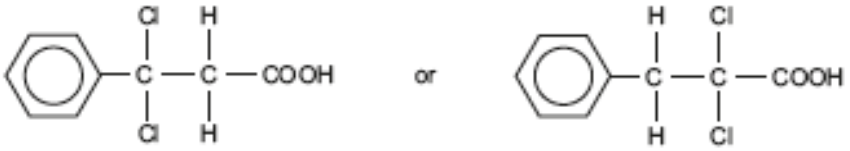
(ii) The bond between the ring and the chlorine atom is stronger than the aliphatic C–Cl bond or vice versa (1)
This is due to interaction between a **lone pair** of electrons on the chlorine atom and the ring electrons (1) [2]

(c) Compound 1 cannot give the m/z fragment value 77 ($C_6H_5^+$) (1)

Compound 2 has a chiral centre (1)

Compound 3 is rapidly hydrolysed by water / has a chiral centre (1)

Possible correct answers



(1)

[4]

QWC Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning [1]

Total [20]

5. (a) Number of moles of nitrogen = 1.00/23.2 = 0.0431 (1)
thus number of moles of the amine is also 0.0431

M_r of the amine = mass / number of moles = 2.54 / 0.0431 = 58.9 (1)

$R — NH_2 \longrightarrow 58.9$

16.02 ∴ R = '43' ∴Formula is $CH_3CH_2CH_2NH_2$ or $(CH_3)_2CHNH_2$ (1) [3]

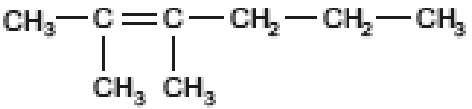
(b) (i) An electron deficient species that seeks out an electron rich / negatively charged / δ- site in a molecule [1]

(ii) 3-methylphenylamine [1]

(iii) These types of group are called **chromophores / azo** (1)
and are responsible for the production of colour in compounds as found in **azo-dyes** (1) [2]

(c) (i) Nucleophilic addition and elimination / condensation (1)
The products are orange/ red/ yellow (1) [2]

(ii) R_f values 2.5 / 7.2 = 0.35 and 3.5 / 7.2 = 0.49 (1)
Ketones are propanone and pentan-2-one (1)

Alkene **W** is  (1)

The name is 2,3-dimethylhex-2-ene (1) [4]

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

(iii) The equation / information shows that R and R^1 are different alkyl groups.
2-methyl-3-ethylpent-2-ene has both R and R^1 as ethyl groups [1]

(d) (i) $CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$ [1]

(ii) Mass of ethanoic acid = 0.45 × 60 = 27 g [1]

(iii) There is no indication of the time necessary to reflux the mixture / method of heating / mention of dangers from fire [1]

(iv) It acts as a catalyst / dehydrating agent / necessary to remove water / move the position of equilibrium to the right [1]

(v) To react with (any remaining) ethanoic acid [1]

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A Level

1094/01

S16-1094-01

CHEMISTRY – CH4

P.M. TUESDAY, 14 June 2016

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**12**	
	2.	**13**	
	3.	**15**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1094 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

Examiner only

SECTION A

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

1. *(a)* A compound **P** of molecular formula $C_4H_{10}O$ was heated with acidified potassium dichromate(VI). The solution changed from orange to green and compound **Q**, of molecular formula C_4H_8O, was formed. Compound **Q** had no effect on Tollens' reagent.

(i) Name the **type** of reaction that occurred when compound **P** was heated with acidified potassium dichromate(VI). [1]

.....

(ii) State what information the lack of reaction with Tollens' reagent gives. [1]

.....

(iii) When compound **P** was heated with concentrated sulfuric acid a mixture of three isomers formed. All these isomers decolourised bromine.

I. Name the **type** of reaction that occurred when compound **P** was heated with concentrated sulfuric acid. [1]

.....

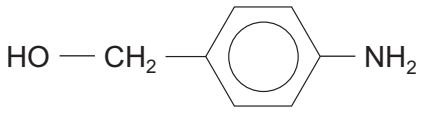
II. Draw the structural formulae of the **three** isomers formed. [3]

(iv) Draw the **skeletal** formula of compound **P**. [1]

Examiner only

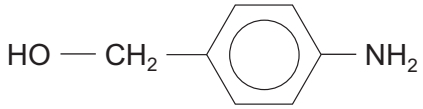
(b) Primary amines contain the functional group NH_2. For each of the reactions below identify the organic product(s).

(i) The reaction between compound **S** and cold nitric(III) (nitrous) acid. [1]



compound **S**

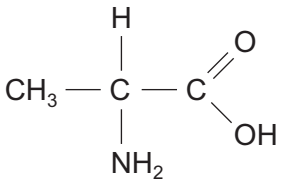
(ii) The reaction between compound **S** and ethanoyl chloride (CH_3COCl). [2]



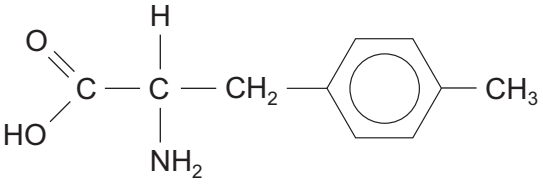
compound **S**

Examiner only

(iii) The reaction between compound **T** and compound **U** (forming two dipeptides). [2]



compound **T**



compound **U**

Total [12]

12

Examiner only

2. Students in an A level chemistry group were discussing topics that they had studied. They decided that each of the following statements was incorrect.

For each statement:

- identify the error and explain why the statement is incorrect,
- discuss the chemical principles involved, naming the products of any reaction.

(a) Ethanol and propanone can be distinguished from each other because only propanone forms a yellow solid when warmed with iodine and aqueous sodium hydroxide. [4]
QWC [1]

(b) Bubbles are formed when carboxylic acids or phenols are added to aqueous sodium carbonate. [4]

(c) *α*-amino acids are solids at room temperature whereas small carboxylic acids and small amines are liquids. The higher than expected melting temperatures of the *α*-amino acids is due to the presence of hydrogen bonds. [4]

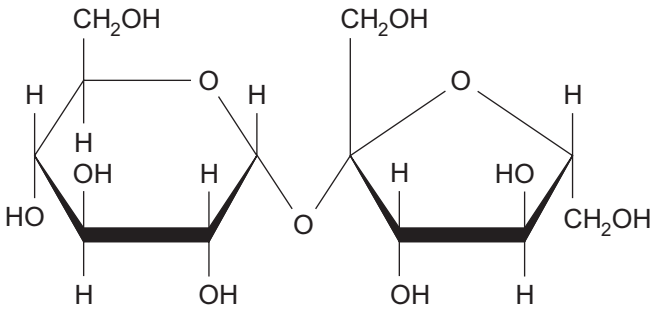
Total [13]

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

Stereoisomerism in organic compounds

Stereoisomerism in organic compounds often involves the presence of a chiral centre but this is not always the reason for different isomers being possible. The existence of stereoisomers can be useful but it can have serious effects in biological systems.

Sucrose is a sugar with the formula below.



Sucrose can be hydrolysed to produce two simpler sugars – glucose and fructose. The hydrolysis of sucrose can be carried out by merely heating the sugar with water but it is much quicker if an enzyme or an acid is used as a catalyst. The extent to which hydrolysis has occurred can be followed using the fact that sucrose does not contain an aldehyde group but glucose and fructose both exist in a form that includes this functional group.

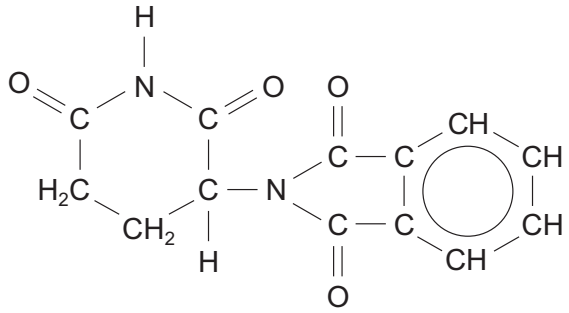
The hydrolysis can also be monitored by using the fact that sucrose, glucose and fructose all exist in forms that are optically active. The table shows data for this optical activity.

Sugar	Angle of rotation for 1 mol dm^{-3} solution
sucrose	+66.5°
glucose	+52.8°
fructose	−92.0°

The solution that is formed after the complete hydrolysis of sucrose is called invert sugar.

Examiner only

15 Thalidomide is a drug that has a wide range of valuable medical uses. Its formula is below.



This molecule contains a chiral centre and therefore has two optical isomers. One of the isomers is safe but the other one is dangerous to the foetus if taken by pregnant women. It is possible to prepare only the safe isomer but, in the body, a racemic mixture is produced.

- End of passage -

(a) What is *stereoisomerism*? *(line 1)* [1]

.....

.....

(b) Suggest a chemical method by which an analytical chemist could identify that sucrose has been hydrolysed. *(line 8)* [2]

.....

.....

.....

(c) (i) Explain what is meant by *optical activity* and the significance of the sign in the table of data. *(line 12)* [2]

.....

.....

.....

(ii) Use the data to explain why a rotation of −39.2° is seen when the hydrolysis of sucrose is complete. [2]

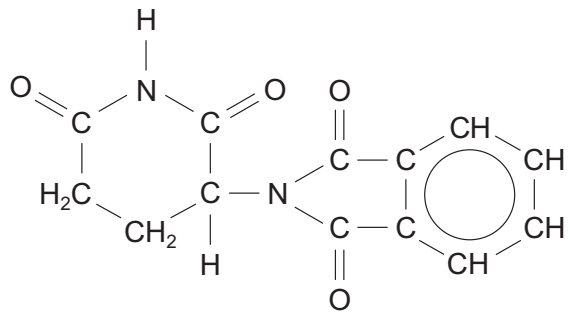
.....

.....

.....

Examiner only

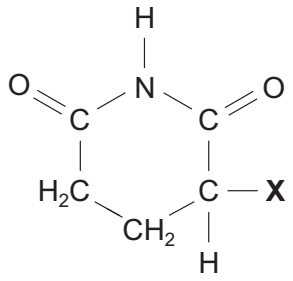
(d) Mark with an asterisk (*) the chiral centre on the thalidomide molecule below. [1]



(e) State what happens when a racemic mixture is formed from a sample containing only one isomer. *(lines 17-19)*

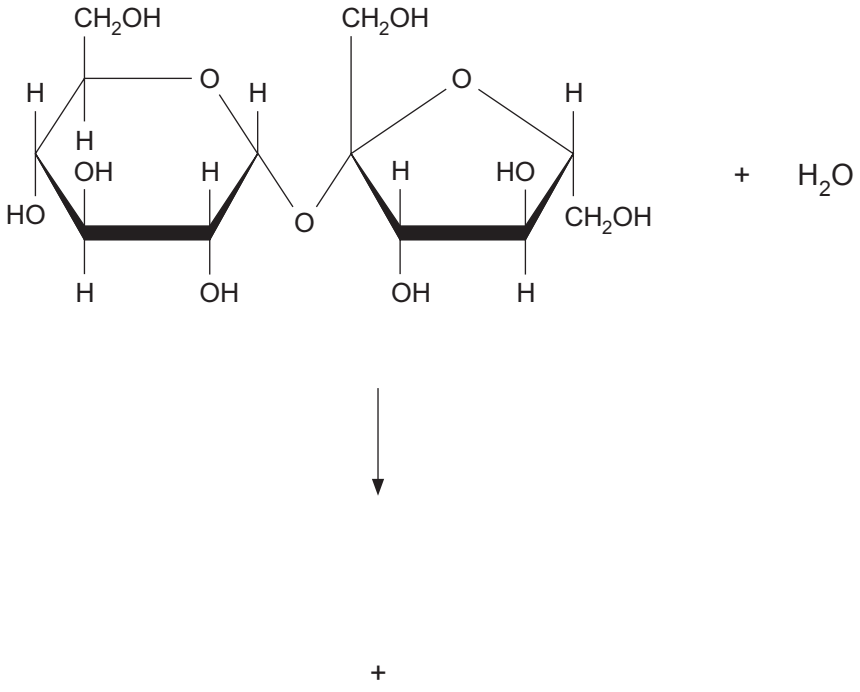
You should include suitable diagrams of a simple molecule of your choice. [2]

(f) The formula below shows part of the thalidomide molecule (with the other part being replaced by the letter **X**). Draw the structural formula of a product formed when this molecule is heated with dilute aqueous hydrochloric acid. [2]



Examiner only

(g) (i) Complete the equation to show clearly the difference in structure between glucose and fructose. You do **not** need to state which structure is which isomer. *(line 6)* [1]



(ii) Explain why sucrose, glucose and fructose are all very soluble in water. [2]

.....

.....

.....

Total [15]

15

Total Section A [40]

SECTION B

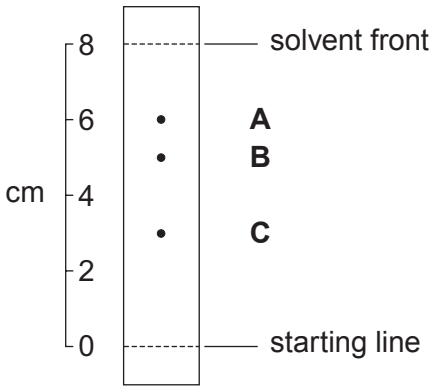
Answer **both** *questions in the separate answer book provided.*

4. There are many different types of chromatography and spectroscopy that can be used to investigate the identity and structure of unknown substances. In this question you will consider some of these techniques.

(a) Explain briefly how the peaks in NMR spectra and the absorptions in IR spectra are formed. [3]

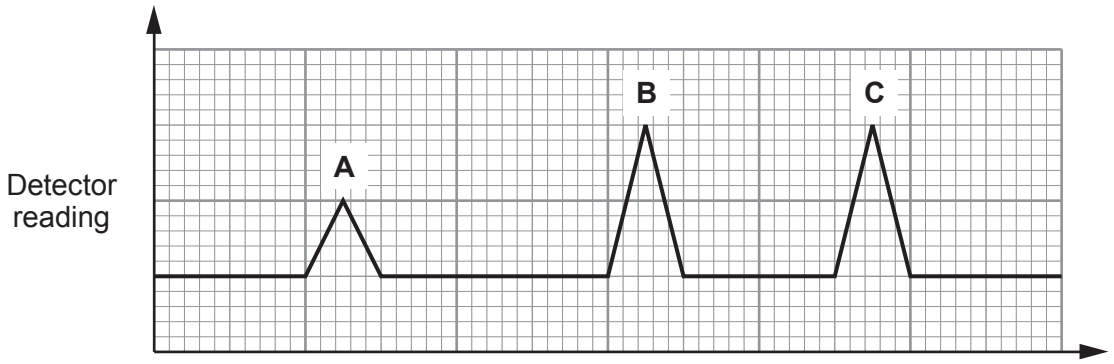
(b) A sample of unknown substances was investigated using different chromatographic techniques.

(i) Thin layer chromatography gave the chromatogram shown below.



Calculate the R_f value for the substance that gives the spot labelled **B**. [1]

(ii) Gas chromatography gave the chromatogram shown below.

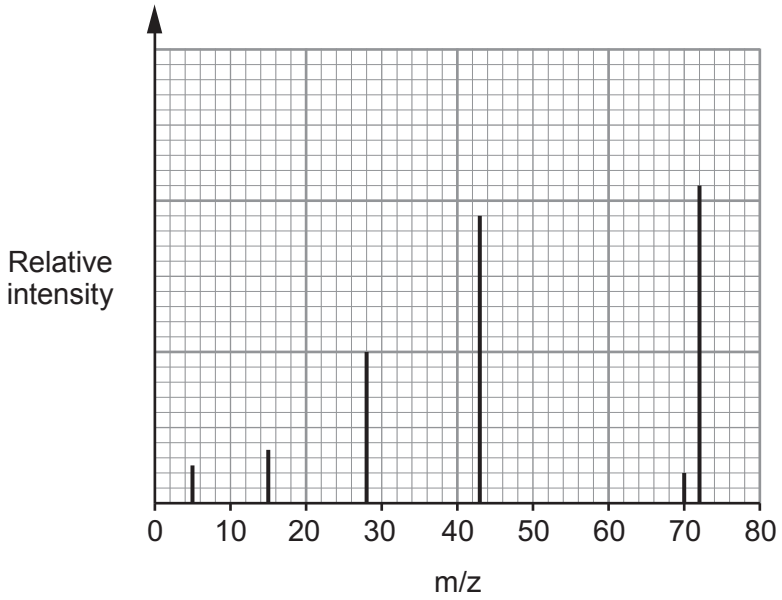


I. What label should be used for the x-axis? [1]

II. Use the chromatogram to estimate the percentage of compound **A** in the sample. Explain how you reached this conclusion. [2]

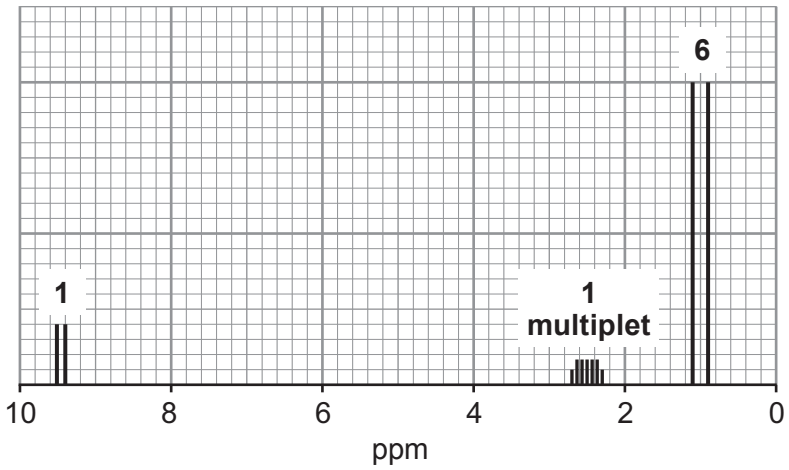
(iii) Thin layer chromatography and gas chromatography give different information about unknown substances. Describe what information can be obtained from each type of chromatography. [2]

(c) (i) A compound **Y** contains carbon, hydrogen and oxygen. It has 66.7 % by mass of carbon. The mass spectrum of compound **Y** is below.



Use these data to determine the molecular formula of compound **Y**. Explain your reasoning. [4]

(ii) The NMR spectrum of compound **Y** is below.



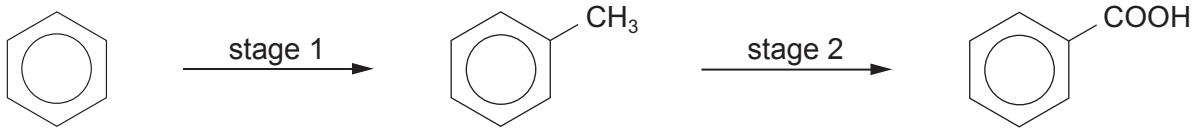
Use this spectrum to determine as much information as possible about the structure of compound **Y**. [4]

QWC [2]

(iii) Use your answers to parts (i) and (ii) to give the structural formula of compound **Y**. [1]

Total [20]

5. Benzene can be made into benzenecarboxylic acid (benzoic acid) using a two-stage process.



(a) Stage 1 proceeds using a mechanism that is similar to that of the halogenation of benzene. Describe the reaction in stage 1. You should include

- the reagent(s) needed
- the type of reaction
- the conditions needed
- details of the mechanism. [7]

(b) Stage 2 involves refluxing methylbenzene with alkaline potassium manganate(VII), filtering the mixture whilst it is still hot and then adding hydrochloric acid. This produces a white precipitate of benzoic acid.

(i) Explain what is meant by *reflux*. [2]

(ii) Write the **balanced** equation for the reaction in stage 2 – the oxidation of methylbenzene to benzoic acid. Use [O] to represent alkaline potassium manganate(VII). [1]

(iii) Apart from neutralising any excess alkali, why is hydrochloric acid added after filtration? [1]

(iv) Benzoic acid is very much more soluble in hot water than it is in cold water. Use this fact to describe how you would purify the benzoic acid produced in stage 2. [3]

(v) Describe a method to show if the benzoic acid is now pure. [1]

(vi) A student used 10.0 g of benzene to prepare benzoic acid as described above. He obtained 3.8 g of pure benzoic acid. Calculate the percentage yield of this process. [3]

(vii) The percentage yield obtained in this particular preparation is usually low. Describe **two** reasons why this percentage yield is low, even if the reaction is carried out carefully. [2]

Total [20]

Total Section B [40]

END OF PAPER

GCE A level

1094/01-A

S16-1094-01A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. TUESDAY, 14 June 2016

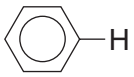
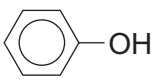
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

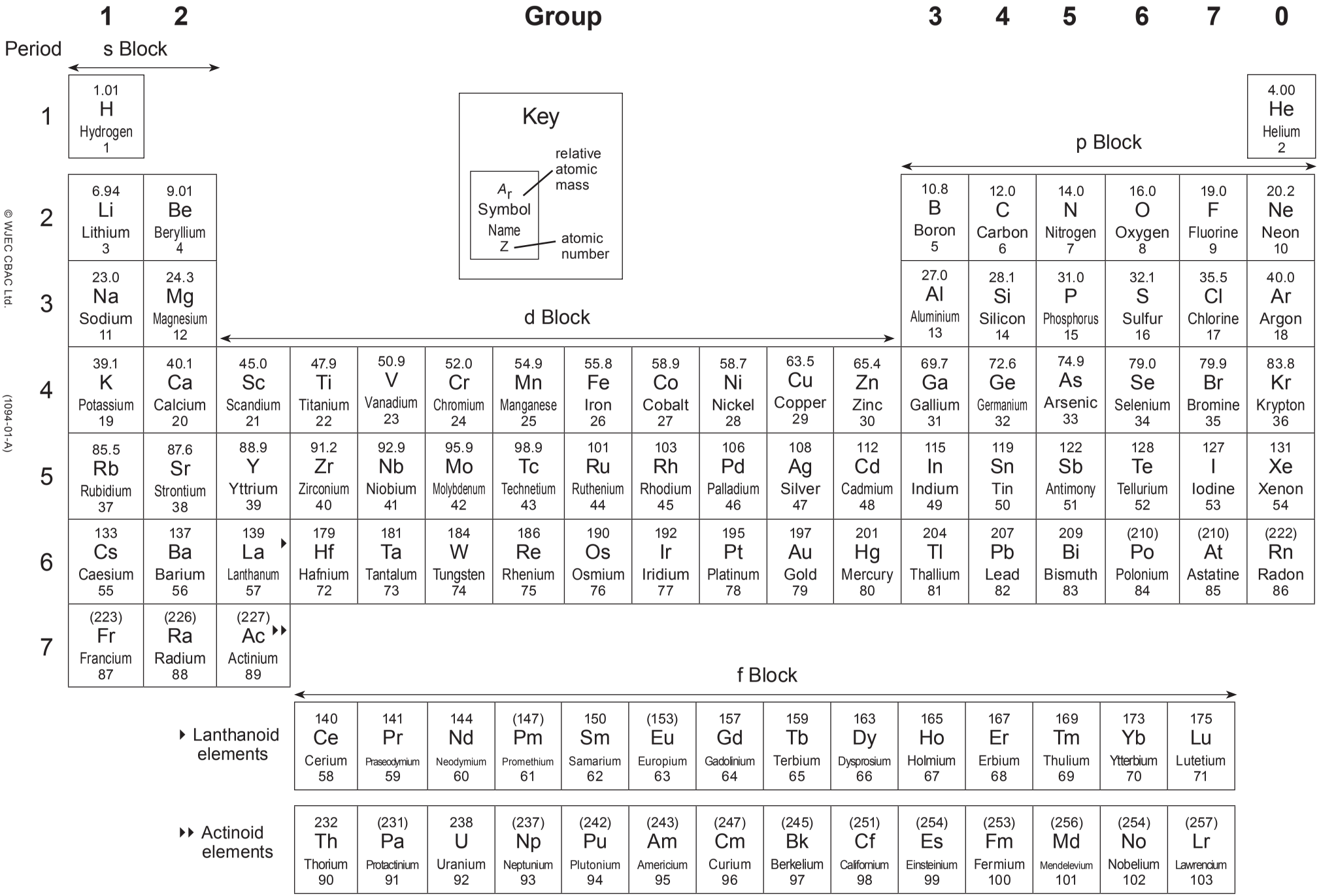
Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
CH_3-CCl_2-	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$R-CCl_2-CH_2-C(=O)-Cl$	2.5 to 3.0
$R-CH_2-Cl$	3.3 to 4.3
$R-OH$	4.5 *
$CH_2=C<$	4.8
	6.5 to 7.5
	7.0 *
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

THE PERIODIC TABLE



GCE MARKING SCHEME

SUMMER 2016

CHEMISTRY - CH4
1094-01

INTRODUCTION

This marking scheme was used by WJEC for the 2016 examination. It was finalised after detailed discussion at examiners' conferences by all the examiners involved in the assessment. The conference was held shortly after the paper was taken so that reference could be made to the full range of candidates' responses, with photocopied scripts forming the basis of discussion. The aim of the conference was to ensure that the marking scheme was interpreted and applied in the same way by all examiners.

It is hoped that this information will be of assistance to centres but it is recognised at the same time that, without the benefit of participation in the examiners' conference, teachers may have different views on certain matters of detail or interpretation.

WJEC regrets that it cannot enter into any discussion or correspondence about this marking scheme.

GCE CHEMISTRY - CH4

SUMMER 2016 MARK SCHEME

SECTION A

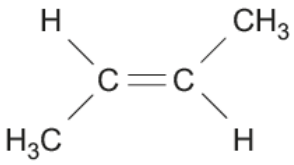
1. *(a)* (i) Redox / oxidation of **P** [1]

(ii) **Q** is not an aldehyde / **P** is not a primary alcohol / **P** is a secondary alcohol [1]

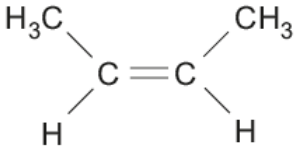
(iii) I Dehydration / elimination [1]

II

(1)

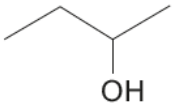


(1)

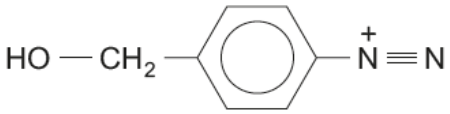


(1)

[3]

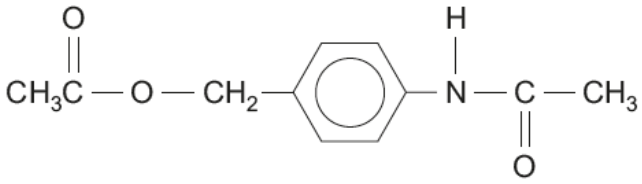
(iv)  [1]

(b) (i)



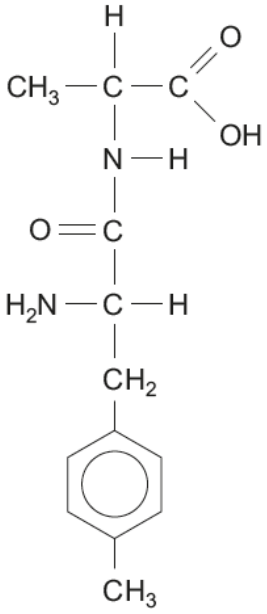
[1]

(ii)

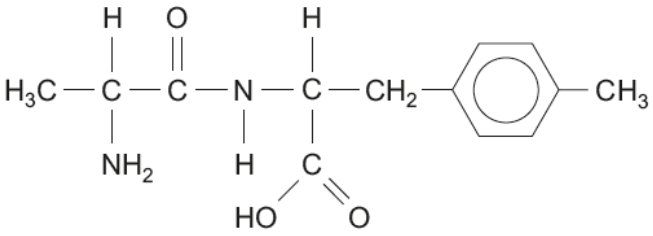


(1) for ester (1) for amide [2]

(iii)



(1)



(1)

accept any unambiguous correct structures

[2]

Total [12]

2. *(a)* **Both** ethanol and propanone will give a yellow solid (1)

Solid is CHI_3/ triiodomethane (1)

Caused by $CH_3C{=}O$ in propanone (1)

Caused by CH_3CHOH in ethanol / ethanol forms $CH_3C{=}O$ (1)

Award (1) for identification of both groups without links to propanone and ethanol [4]

QWC *Legibility of text; accuracy of spelling punctuation and grammar; clarity of meaning* [1]

(b) Carboxylic acids react but phenols do not (1)

Bubbles are carbon dioxide (1)

Carboxylic acids stronger acids than phenols (1)

Carboxylate more stable than phenoxide / O—H bond weaker in carboxylic acid (1) [4]

(c) Hydrogen bonds are not responsible for the higher than expected melting temperature (1)

Results from ionic bonds between zwitterions (1)

High melting temperatures imply the presence of strong <u>intermolecular</u> forces - accept any link between melting and intermolecular forces (1)

Formula of any zwitterion shown unambiguously /
presence of NH_3^+ and CO_2^- /
description of proton transfer from COOH to NH_2 (1)

[4]

Total [13]

3. *(a)* (The existence of more than one compound) with the same structural formula but a different arrangement in space [1]

(b) Fehling's solution (1)

Observe red solid formed (1)

OR

Tollens' reagent (1)

Observe silver mirror (1) [2]

(c) (i) (Optical activity occurs when different isomers) rotate the plane of plane polarised light (1)

(Values have) opposite signs since rotation is in opposite directions (1)

[2]

(ii) When hydrolysis is complete there will be equal amounts of glucose and fructose (1)

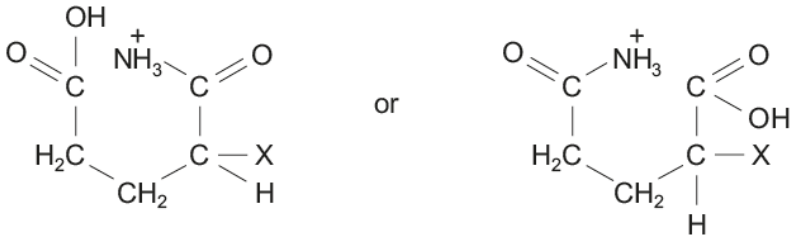
Clear use of + 52.8 and –92.0 to give –39.2 (1) [2]

(d) Asterisk on C attached to CH_2, CO, N and H [1]

(e) Equimolar amounts of two isomers formed/ half the original changes to the other isomer (1)

3D diagrams to show mirror images of **any** chiral centre (1) [2]

(f)



NH_3^+ in correct formula (1)

COOH in correct formula (1)

[Allow two —COOH groups (1) and NH_3/ NH_4^+ (1)] [2]

(g) (i) $C_6H_{12}O_6$ shown twice [1]

(ii) All contain lots of OH groups (1)

That can hydrogen bond to water (1) [2]

Total [15]

SECTION B

4. *(a)* Any 3 from:

Energy absorptions / transitions / jumps in either NMR or IR (1)

NMR – involves proton spin aligned with or against (1)

Magnetic field (1)

IR – bonds / molecules vibrate / stretch / bend (more) (1)

Max 2 if only NMR or IR considered [3]

(b) (i) R_f = 0.62 – 0.63 [1]

(ii) I Retention time [1]

II Use of area under peaks/ heights of peaks (1)

20% (answer showing correct use of area under peaks) (1)
[2]

(iii) TLC shows number of components in the mixture (1)

Gas chromatography shows (number of components and) amounts / relative abundance of each component (1)

[2]

(c) (i) Molecular ion is at 72 / M_r is 72 (1)

Mass of C in 1 mol = $\frac{66.7 \times 72}{100}$ = 48 (1)

24 difference so only one oxygen atom possible / recognition of fragment containing one oxygen atom – CO at 28 or CH_3CO at 43 (1)

C_4H_8O (1) [4]

(ii) 3 hydrogen environments (1)

Number of Hs in each environment 1:1:6 (1)

Doublet produced by H next to C with 1 attached H/

multiplet produced by H next to C with many Hs (1)

Any **two** δ values:

δ = approximately 1 for CH_3

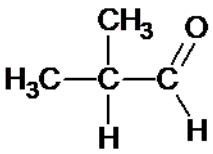
δ = 2.0 to 2.5 for CH_3CO (accept CH_2CO)

δ = approximately 9.5 for HC=O (1) [4]

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

Organisation of information clearly and coherently; use of specialist vocabulary (1) [2]

(iii)



[1]

Total [20]

5. *(a)* Reagent: chloromethane (1)

Type of reaction: electrophilic substitution (1)

Conditions: aluminium chloride/ iron(III) chloride (catalyst) (1)

Mechanism: equation to show formation of CH_3^+ (1)

arrow from π bond towards CH_3^+ (1)

structure of intermediate (1)

arrow from bond on H to reform π (1) [7]

(b) (i) (Process involving continuous) evaporation and condensing (1)

(Achieved using) vertical condenser/ avoids losing liquids (during continuous heating) (1) [2]

(ii) $C_6H_5CH_3 + 3[O] \rightarrow C_6H_5COOH + H_2O$ [1]

(iii) To add H^+ to COO^- / to replace Na^+ in COO^-Na^+ /
to form acid from salt / strong acid displaces weak acid [1]

(iv) Dissolve solid in <u>minimum</u> of hot water / solvent (1)

Allow to cool (to crystallise solid) (1)

Filter and dry (1) [3]

(v) Melting temperature same as literature value /
melting temperature sharp/ melts not over range

OR

Chromatography – produces only one peak / reading [1]

(vi) M_r C_6H_6 = 78 and C_6H_5COOH = 122 (1)

10.0g C_6H_6 = 10.0/78 = 0.128 mol **and**

should produce 0.128 × 122 = 15.6 g C_6H_5COOH (1)

Percentage yield = 3.8 × 100/ 15.6 = 24(.4)% (1) [3]

(vii) Any 2 from:

Incomplete oxidation/ formation of aldehyde (1)

Solid left in solvent during recrystallisation (1)

Two-stage process so losses at both stages (1)

Multiple alkylation possible (1) [2]

Total [20]