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**	

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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]

.....

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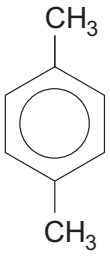
(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.



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]

.....

.....

.....

.....

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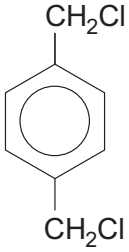
(d) 1,4-Dimethylbenzene reacts with chlorine in a free radical reaction to give the liquid 1,4-di(chloromethyl)benzene.



(i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

Method 1 .....

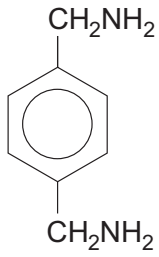
Method 2 .....

(ii) Give the displayed formula of the compound produced when 1,4-di(chloromethyl)benzene reacts with an excess of aqueous sodium hydroxide. [1]

Turn over.

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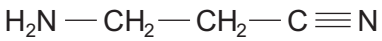
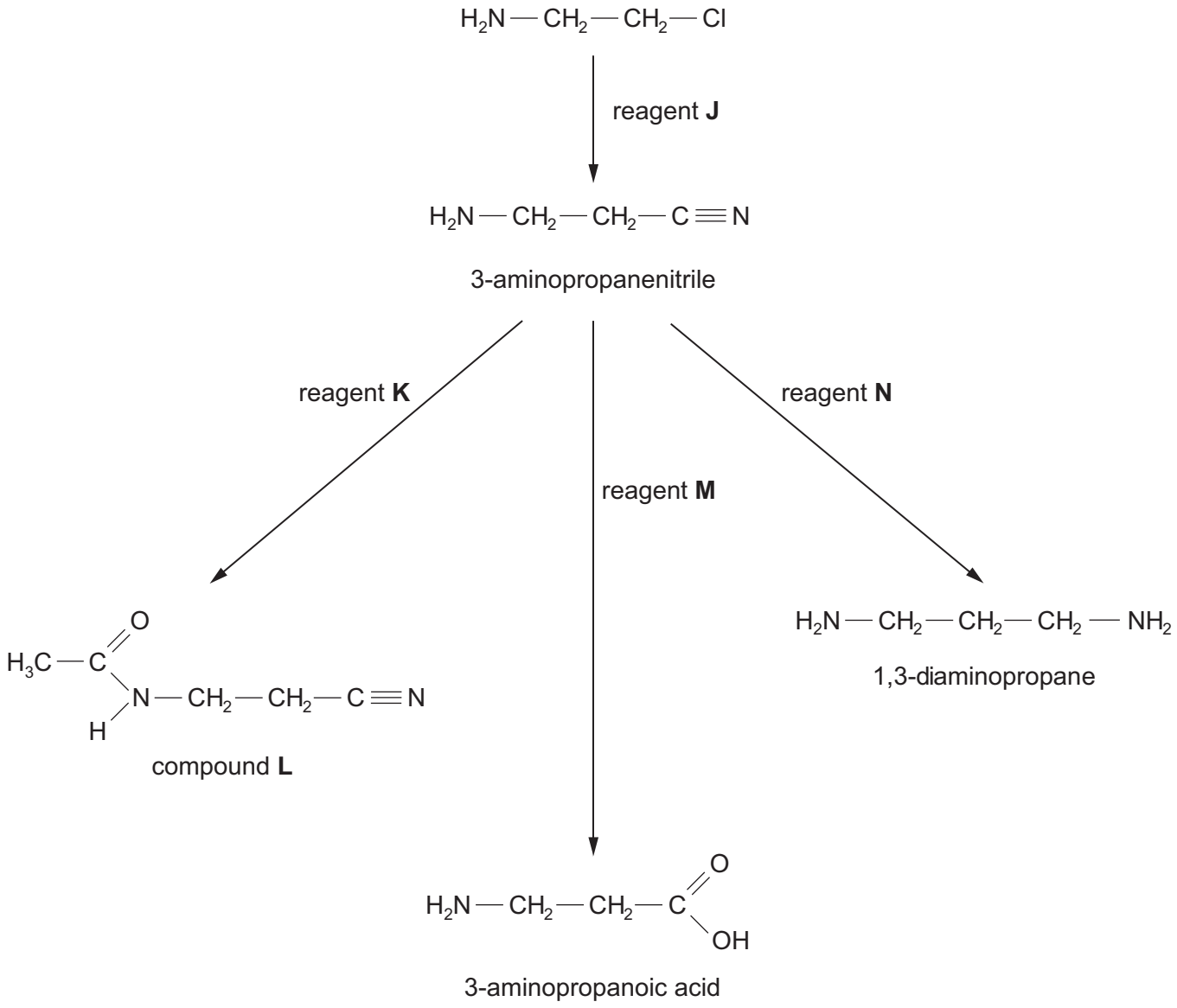
2. *(a)* Seeds of the sweet pea plant contain 3-aminopropanenitrile.



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



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(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]

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(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]

.....

.....

Turn over.

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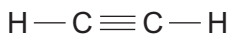
3. *Read the passage below and then answer the questions in the spaces provided.*

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.

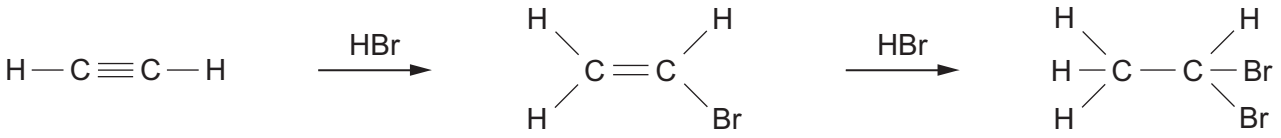
$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

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.

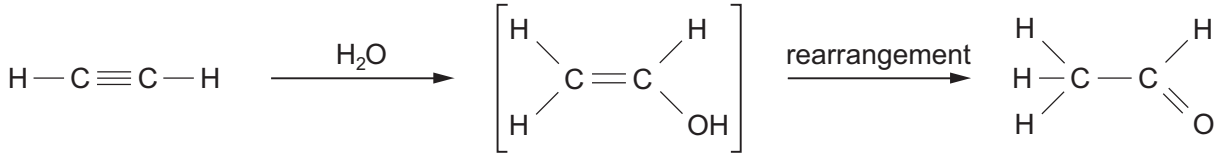
$$CH_2{=}CH_2(g) \rightleftharpoons C_2H_2(g) + H_2(g)$$

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

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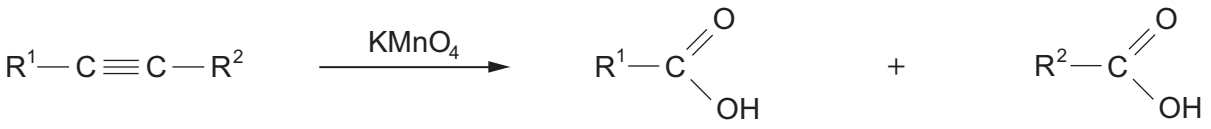
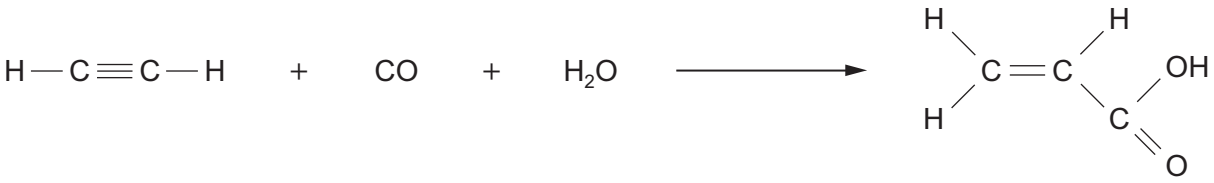
The oxidation of ethyne to carbon dioxide and water is the chemical basis of oxy-acetylene welding. If an alkyne is less strongly oxidised by using potassium manganate(VII) solution under suitable conditions the C ≡ C bond is broken to give carboxylic acids.



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]

.....

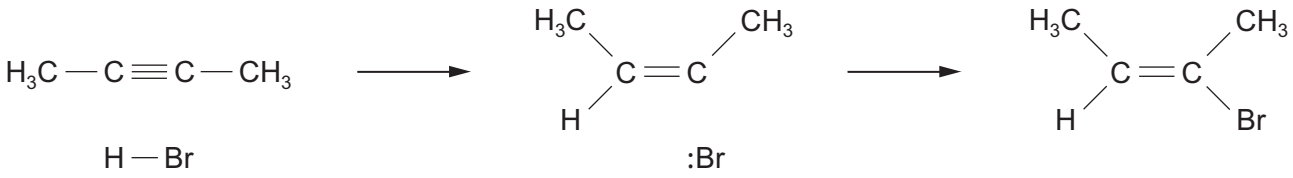
.....

Turn over.

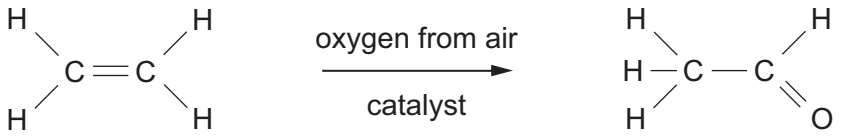
Examiner only

(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

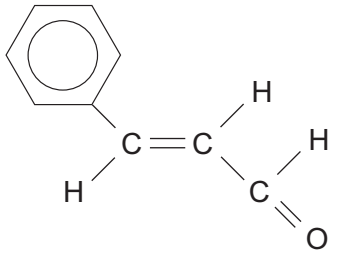
Total Section A [40]

Turn over.

SECTION B

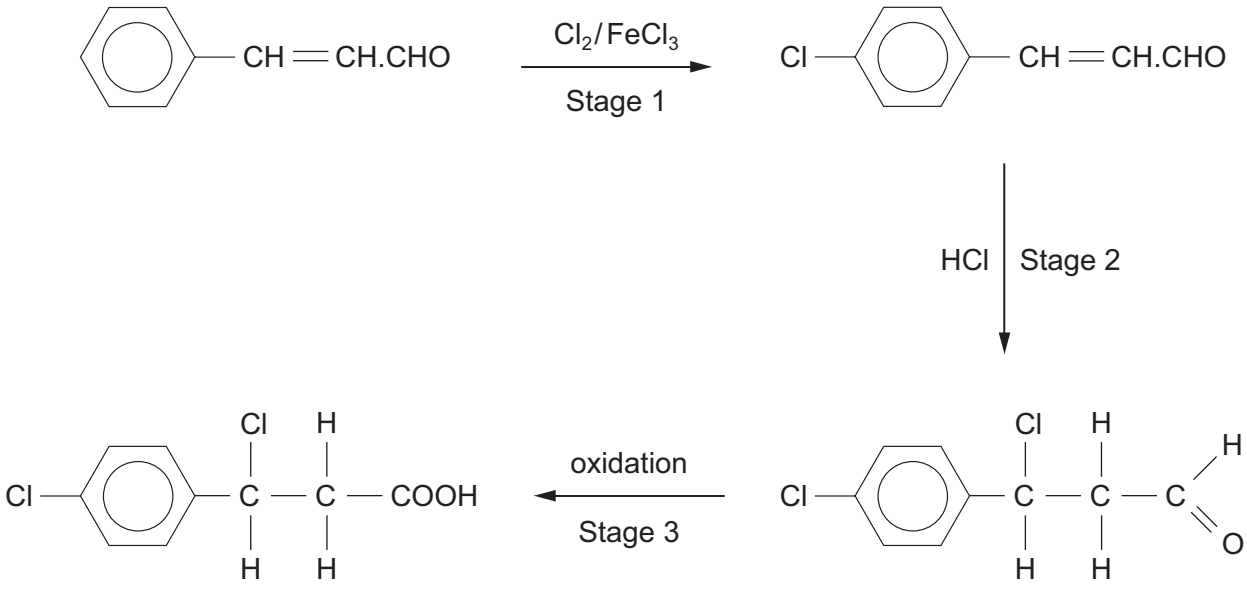
Answer **both** *questions in the separate answer book provided.*

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]

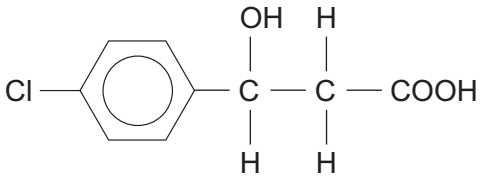
QWC [1]

(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.

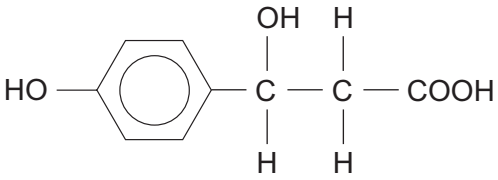
(i) A sample is added to aqueous sodium hydrogencarbonate. State what is seen during this reaction and name the functional group that has been confirmed. [2]

(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**

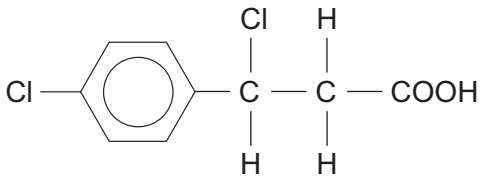
Explain why compound **N** is formed in preference to compound **P**.



compound **P**

[2]

(c) Compound **R** is an isomer of compound **M** (whose formula is shown below).

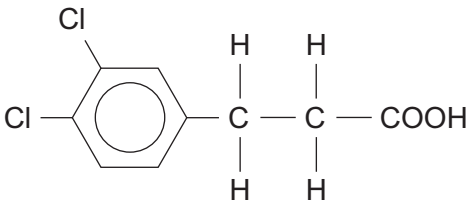


compound **M**

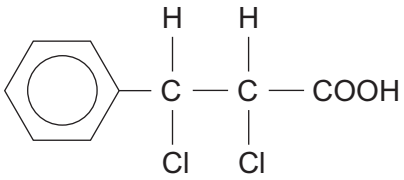
Tests on compound **R** show that it:

- 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.

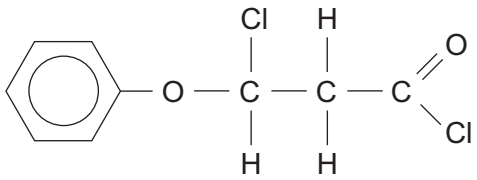
Three compounds that do **not** fit this information are shown below.



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]

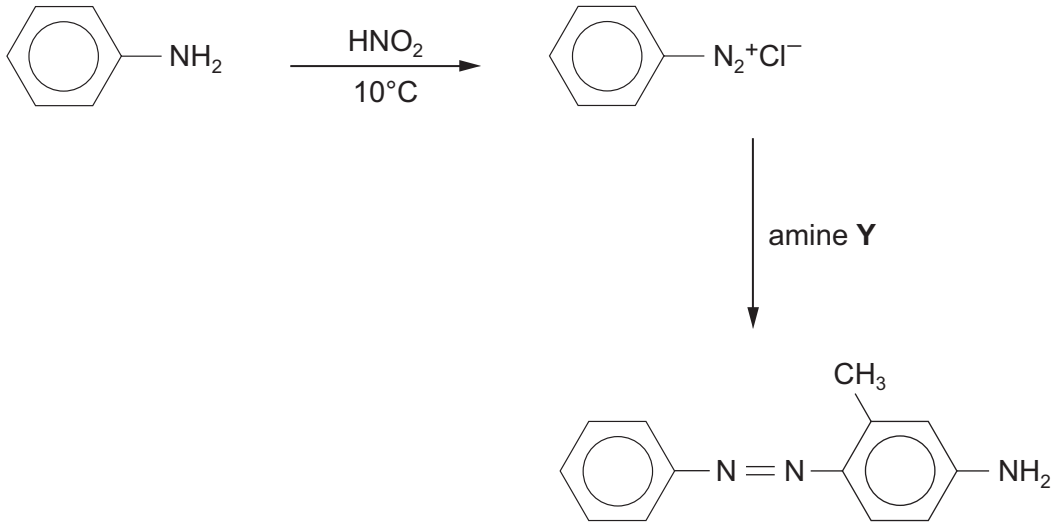
5. *(a)* Primary aliphatic amines react with nitric(III) (nitrous) acid to give a quantitative yield of nitrogen gas, and an alcohol as the major organic product.

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.

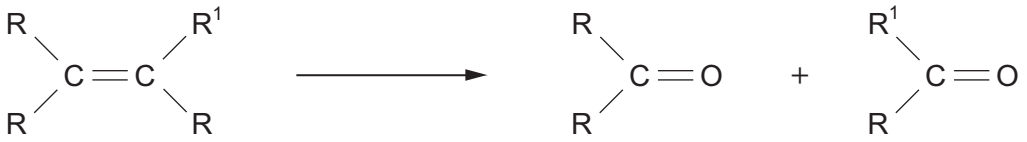


(i) The benzenediazonium ion acts as an electrophile in this reaction.
State the meaning of the term electrophile. [1]

(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.



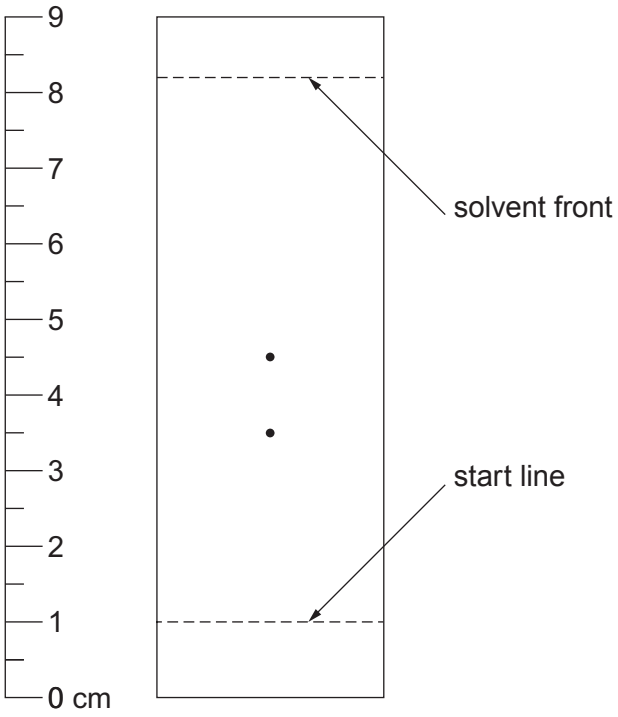
alkene **W**

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]

Turn over.

(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

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S15-1094-01A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 10 June 2015

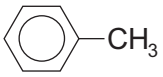
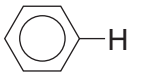
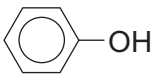
Infrared Spectroscopy characteristic absorption values

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
$CH_3-C(=O)-$	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

Turn over.

THE PERIODIC TABLE