Surname	Centre Number	Candidate Number
Other Names		2

GCE A LEVEL – NEW

1410U40-1

S17-1410U40-1

CHEMISTRY – A2 unit 4
Organic Chemistry and Analysis

MONDAY, 19 JUNE 2017 – MORNING

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 8.**	**10**	
Section B	**9.**	**14**	
	10.	**14**	
	11.	**16**	
	12.	**12**	
	13.	**14**	
	Total	**80**	

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ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

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 **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 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 assessment of the quality of extended response (QER) will take place in **Q.12***(a)*.

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

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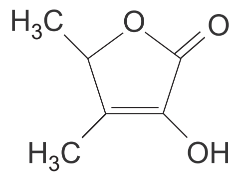
SECTION A

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

1. State what is seen, if anything, when aqueous phenol is added to aqueous solutions of the following reagents. [2]

Reagent	Observation
iron(III) chloride	
sodium hydroxide	

2. Sotolone is one of the compounds that is responsible for the smell of raspberries.

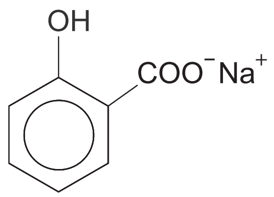


sotolone

Give the **empirical** formula of this compound. [1]

....

3. Complete the equation for the reaction of sodium 2-hydroxybenzoate with soda lime (NaOH), which, on strong heating, can give phenol as one of the products. [1]



$+ \quad NaOH \quad \longrightarrow$

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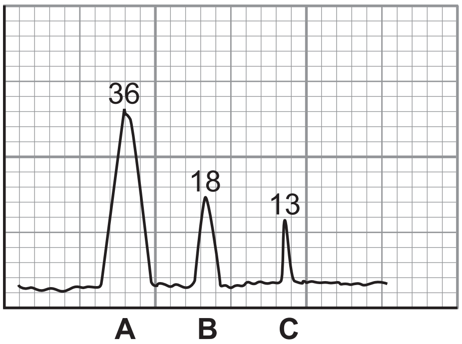
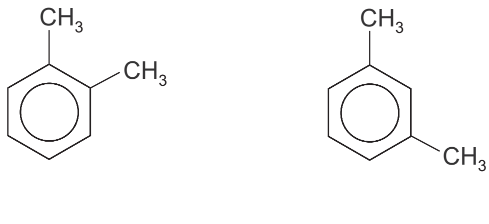
4. State the reagent used to produce phenylmethanol from benzaldehyde. [1]

....

5. The gas chromatogram shows peaks for the products formed by the Friedel-Crafts alkylation of methylbenzene at 0 °C.





A **B** **C**

Use the data to calculate, to the appropriate number of significant figures, the percentage of 1,3-dimethylbenzene, which is present in the products. [1]

Percentage = ... %

6. Give the systematic name of a compound of formula $C_5H_{10}O_2$ that gives propan-1-ol as one of the products when it is warmed with aqueous sodium hydroxide. [1]

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7. Give the displayed formula of the organic compound obtained when cyclohexanol ($C_6H_{11}OH$) reacts with ethanoyl chloride. [1]

8. State the reagents necessary to convert hexane-1,6-diamine to hexane-1,6-dioic acid in two stages. [2]

$$H_2N(CH_2)_6NH_2 \xrightarrow{\textbf{A}} HO(CH_2)_6OH \xrightarrow{\textbf{B}} HOOC(CH_2)_4COOH$$

A ....

B ....

10

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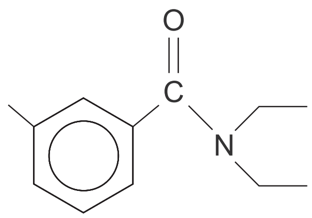
SECTION B

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

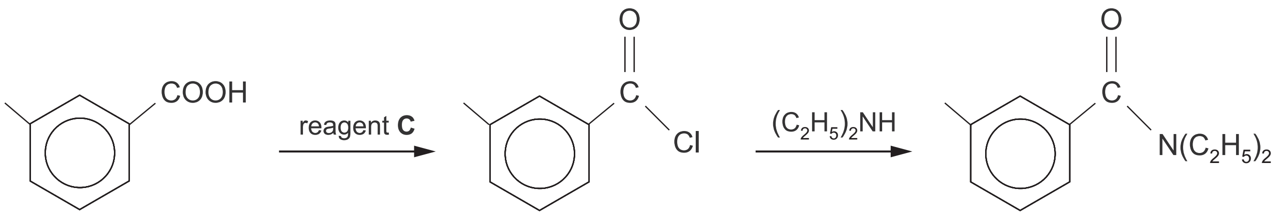
9. Insect repellents are materials that can be applied to the skin or to clothing in order to provide protection against biting insects.

(a) N,N-Diethyl-3-methylbenzamide, commonly known as DEET, has proved to be one of the most effective insect repellents.



DEET

(i) One method of preparing DEET is by the following reaction sequence.



Identify reagent **C** that can be used to convert 3-methylbenzoic acid to 3-methylbenzoyl chloride. [1]

....

(ii) DEET is a colourless liquid in white light.

Explain, in terms of the electromagnetic spectrum, why DEET is colourless. [1]

....

....

(iii) The mass spectrum of DEET shows a molecular ion at m/z 191. It also shows a prominent peak at m/z 91.

Suggest a formula for the fragment that is **lost** so that the remaining fragment has m/z 91. Show your working. [2]

Formula ....

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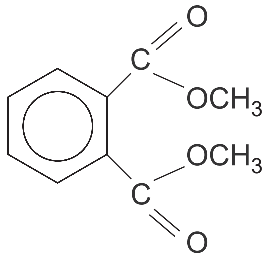
(b) An alternative insect repellent is dimethyl benzene-1,2-dicarboxylate, DMP.



DMP

This can be made by the oxidation of 1,2-dimethylbenzene, followed by acidification of the resulting product and then esterification.

(i) State the oxidising agent used. [1]

....

(ii) Explain why it is necessary to acidify the product of this oxidation. [1]

....

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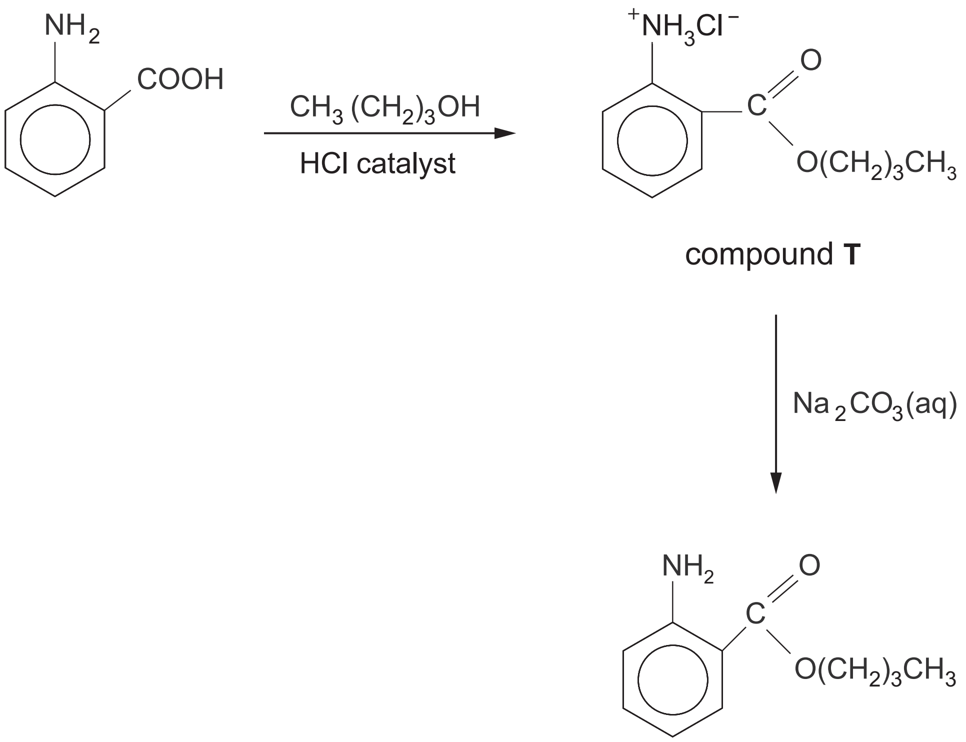
(c) Another insect repellent is the 1-butyl ester of 2-aminobenzoic acid, known as BA. This can be produced from 2-aminobenzoic acid by esterification with butan-1-ol.



1–butyl 2–aminobenzoate (BA)

(i) Draw the zwitterion structure of 2-aminobenzoic acid. [1]

(ii) Explain why compound **T** is initially produced in this reaction. [1]

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(iii) The ester BA is obtained from compound **T** by reacting it with sodium carbonate solution. It is then removed from the mixture by extracting it with the solvent ethoxyethane. After drying the ethoxyethane extract, the solvent is removed by distillation. Ethoxyethane has a boiling temperature of 35 °C and is very flammable.

I. Suggest the origin of the water removed during the drying process. [1]

....

....

II. Suggest how the ethoxyethane solution of BA could be safely heated to remove the solvent. [1]

....

....

(d) There is considerable interest in 'green' methods for the production of organic compounds. Recent studies have shown that BA can be produced from 2-aminobenzoic acid and butan-1-ol at 37 °C, using an enzyme as a catalyst.

(i) In a small scale experiment 4.0×10^{-4} mol of 2-aminobenzoic acid gave a 5 % yield of BA.

Calculate the number of moles of BA that were produced. [1]

n(BA) = ... mol

(ii) The esterification of 2-aminobenzoic acid is a reversible reaction and eventually the mixture will reach equilibrium. Use the information below to suggest why the addition of hexane to the stirred aqueous mixture of reactants increases the yield of the product BA. [3]

- hexane and the aqueous reaction mixture are immiscible
- 2-aminobenzoic acid is more soluble in water than in hexane
- BA is more soluble in hexane than in water

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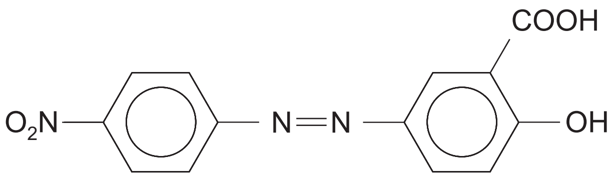
10. *(a)* The azo dye Mordant Orange 1 has the formula shown below.



It is used as a pH indicator for acid-base titrations. At a pH of 10.1 the dye is yellow but at a pH of 12.1 it is orange-red.

(i) Give the displayed formulae of the two starting compounds that react, via a diazonium compound, to give Mordant Orange 1. [2]

(ii) The table shows the colour seen and the colour absorbed for a solution of Mordant Orange 1 as the pH increases.

Colour seen	yellow	orange-red
Colour absorbed	violet	greenish-blue
pH increasing →		

State how the wavelength of the light **absorbed** changes with pH, giving your reasoning. [1]

....

....

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(iii) The visible spectrum of the dye at pH 10.1 shows that it has a maximum absorption at 385 nm.

Calculate the frequency of the radiation being absorbed at 385 nm. [2]

Frequency = ... Hz

(iv) Use your answer to (iii) to calculate the energy of the maximum absorption at 385 nm, giving your answer in kJ mol^{-1}. [3]

Energy = ... kJ mol^{-1}

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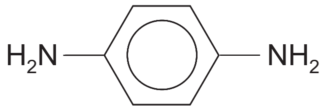
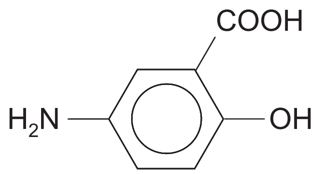
(b) Mordant Orange 1 can be reduced by the enzymes from certain bacteria to produce 1,4-diaminobenzene and 5-amino-2-hydroxybenzoic acid



1,4-diaminobenzene



5-amino-2-hydroxybenzoic acid

(i) 1,4-diaminobenzene can also be made from 4-nitrophenylamine.

State the reagent(s) necessary for this reaction. [1]

....

(ii) Use the displayed formula of 1,4-diaminobenzene to help you describe its ^1H high resolution NMR spectrum. Explain your reasoning.
Reference to the position of the signals is not required. [3]

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(iii) Give the displayed formula of the organic compound formed when 5-amino-2-hydroxybenzoic acid reacts with aqueous sodium hydroxide in a 1:1 molar ratio. [1]

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(iv) 5-Amino-2-hydroxybenzoic acid can be used in medicine to treat a number of conditions. It is believed to work by removing free radicals. One of these radicals is the hydroxyl radical. This can be produced by the homolytic fission of hydrogen peroxide, H_2O_2, where the O—O bond is broken.

Draw a dot and cross diagram of the hydroxyl radical, showing the outer electrons for each atom. [1]

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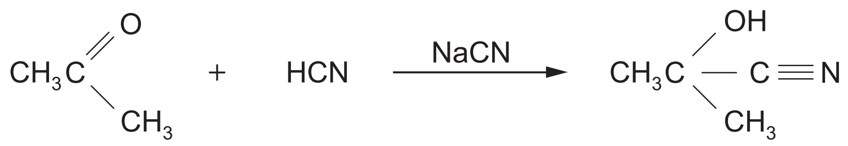
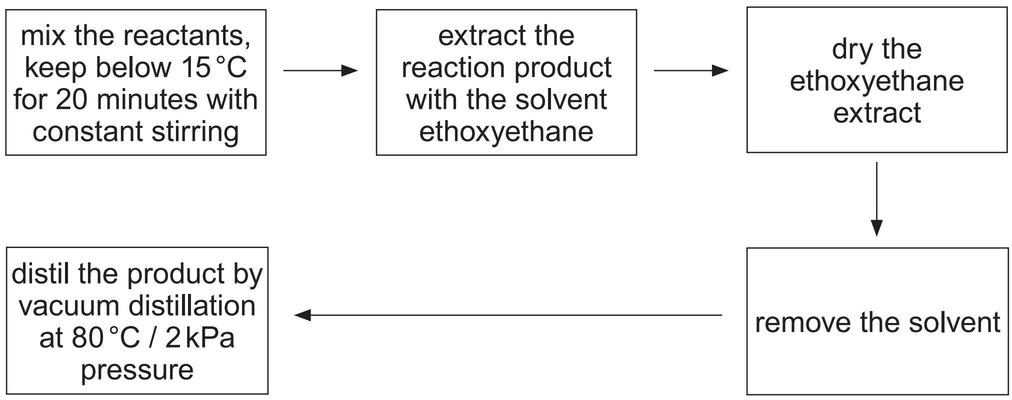
11. *(a)* Propanone reacts with hydrogen cyanide (in the presence of sodium cyanide) to produce 2-hydroxy-2-methylpropanenitrile.



(i) Draw the mechanism for this reaction. Name the type of reaction mechanism occurring. [3]

Mechanism type ....

(ii) The following procedure was suggested to obtain 2-hydroxy-2-methylpropanenitrile.



The overall percentage yield was 55 %.

Suggest **two** stages in the procedure of extraction and distillation that could have resulted in this reduced yield. [2]

1. ....

....

2. ....

....

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(iii) In a further experiment an excess of hydrogen cyanide reacted with 17.4 g of propanone (M_r 58.06) to produce 18.6 g of 2-hydroxy-2-methylpropanenitrile (M_r 85.07).

Calculate the percentage yield of 2-hydroxy-2-methylpropanenitrile. [3]

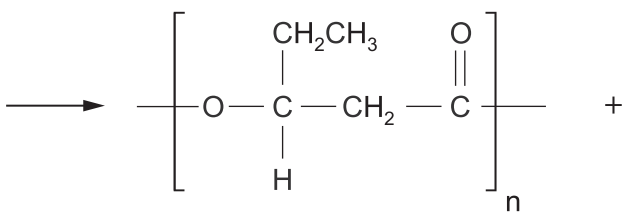
Percentage yield = ... %

(iv) The dehydration of 2-hydroxy-2-methylpropanenitrile produces 2-methylpropenenitrile, $H_2C{=}C(CH_3)CN$. This compound can undergo addition polymerisation giving poly(2-methylpropenenitrile).

Write the formula of the repeating section of this polymer. [1]

(b) There is considerable interest in biodegradable polymers. One of these is the polyester 'polyhydroxyvalerate' (PHV), which is produced from starch or glucose by using microorganisms. One simple chemical way of producing PHV is by the condensation polymerisation of 3-hydroxypentanoic acid.

Complete the equation below, which shows the structure of the repeating polymeric unit. [2]



3-hydroxypentanoic acid

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(c) State **one** difference between condensation polymerisation and addition polymerisation. [1]

....

....

(d) Alcohols react with sodium to give hydrogen gas as one of the products.

$$2R\text{—}OH \quad + \quad 2Na \longrightarrow 2R\text{—}O^{-}Na^{+} \quad + \quad H_2$$

A student thought that the volume of hydrogen given off could be used to identify the alcohol.

In an experiment 0.900 g of the alcohol were dissolved in an inert solvent and an excess of sodium metal was added. 184 cm^3 of hydrogen were collected, measured at 298 K and 1 atm pressure.

(i) The reaction is exothermic. Suggest how the reaction mixture could be maintained at close to room temperature. [1]

....

....

(ii) Use the figures to calculate the relative molecular mass of the alcohol. [2]

M_r = ...

(iii) The alcohol used for this experiment gave a ketone on oxidation.

Give the displayed formula of the alcohol. [1]

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12. *(a)* Queen bees secrete a pheromone, compound **W**, which is used for a number of purposes, both inside and outside the hive.

Compound **W**

- is a straight chain aliphatic compound
- has a relative molecular mass of 184
- contains only carbon, hydrogen and oxygen
- contains 65.2% carbon and 26.1% oxygen by mass
- reacts with an alkaline solution of iodine to give a yellow solid
- produces effervescence when added to sodium hydrogencarbonate solution
- has a C=C double bond between carbons 2 and 3 and is an *E*-isomer
- produces an orange solid when reacted with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens reagent

Use all of this information to suggest a displayed formula for compound **W**. [6 QER]

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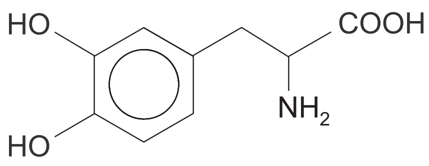
(b) Broad bean plants produce the α-amino acid L-dihydroxyphenylalanine (L-DOPA), which has important uses in the treatment of Parkinson's disease.



L-DOPA

(i) Identify the chiral centre on the formula of L-DOPA by using an asterisk (*). [1]

(ii) A solution containing equimolar proportions of L-DOPA and its enantiomer D-DOPA is described as a racemic mixture.

Explain why this mixture has no apparent effect on the plane of plane polarised light. [2]

....

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(iii) Write the displayed formula of the dipeptide formed from L-DOPA. [1]

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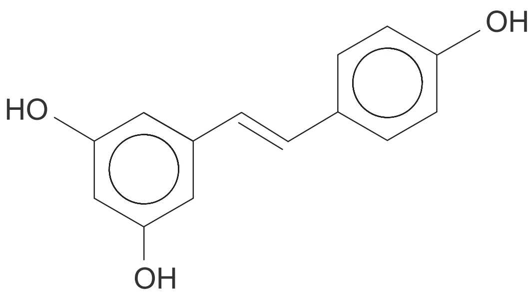
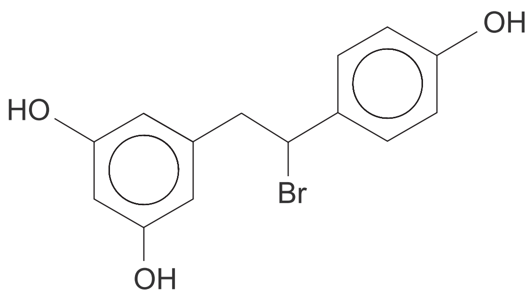
(c) Grape skins contain resveratrol.



resveratrol

(i) The addition of hydrogen bromide to resveratrol results in the compound whose formula is shown below.



Explain why this addition does not involve the aromatic rings. [1]

....

....

(ii) Suggest a displayed formula for a compound produced when excess aqueous bromine is added to resveratrol. [1]

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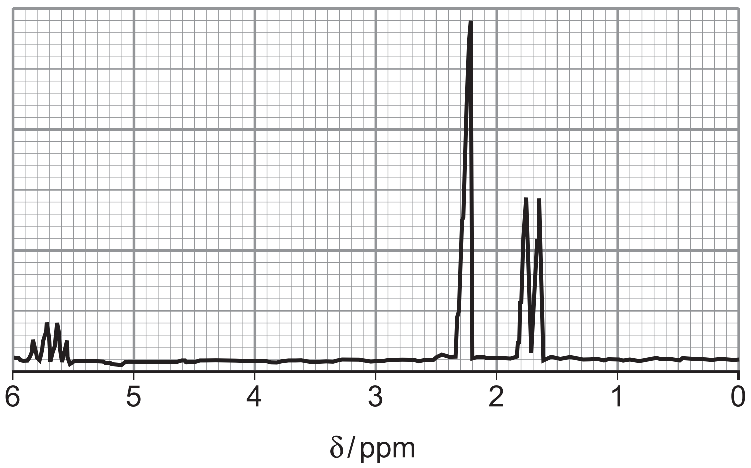
13. *(a)* The analysis of a compound shows that its formula is C_4H_7Br.
The high resolution ^1H NMR spectrum of the compound is shown below.

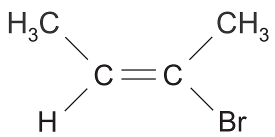


(i) A student suggested that the compound might be one of the following.

compound **L** $BrCH_2—CH_2—CH=CH_2$

compound **M** $CH_3—CH_2—C(Br)=CH_2$

compound **N**



Discuss the splitting pattern seen in the ^1H NMR spectrum to decide whether the compound is **L**, **M** or **N**. Give reasons for your answer. [4]

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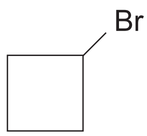
(ii) Another student suggested that the compound was bromocyclobutane.



I. Describe a chemical test that would show that the compound was either **L**, **M** or **N** and not bromocyclobutane. You should state the result of your test with each compound. [1]

....

....

....

II. Explain how the ^{13}C NMR spectrum would show that the compound was **L**, **M** or **N** and not bromocyclobutane. [2]

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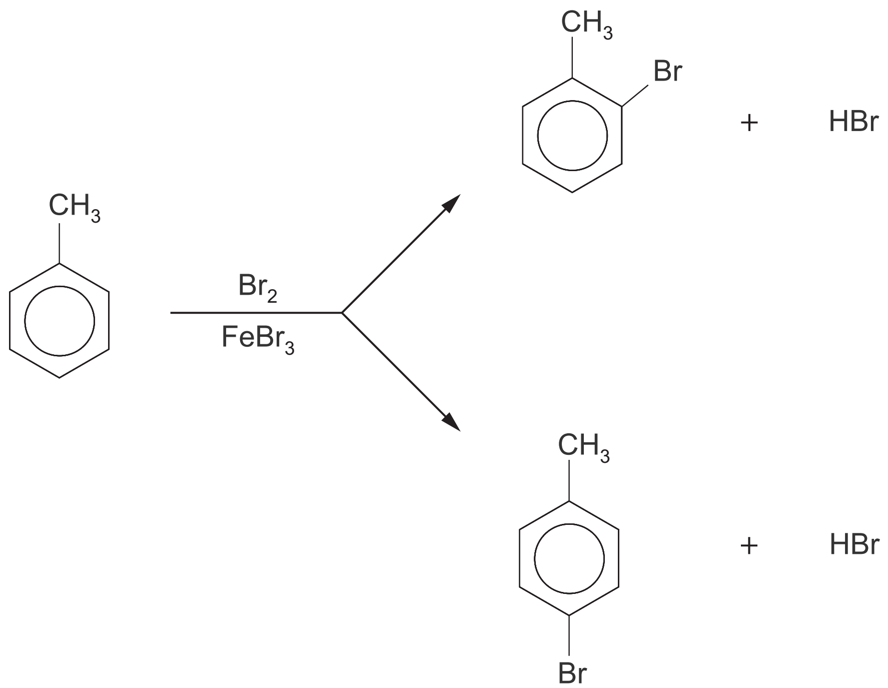
(b) The bromination of methylbenzene using electrophilic substitution gives a mixture of 2-bromomethylbenzene and 4-bromomethylbenzene.



Give the mechanism of the reaction that produces 4-bromomethylbenzene. [3]

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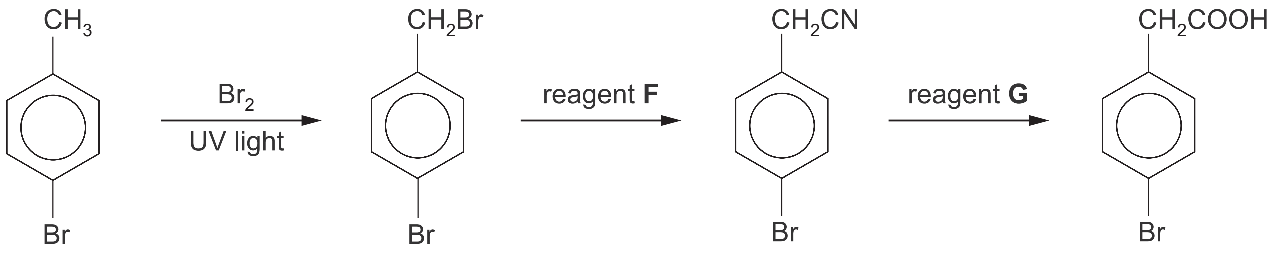
(c) A reaction sequence to produce 4-bromophenylethanoic acid is shown below.



(i) The bromination of 4-bromomethylbenzene is a free radical process.

Give the equation for this reaction and then use the equation to calculate the minimum mass of bromine needed to convert 0.15 mol of 4-bromomethylbenzene to 4-bromo-1-(bromomethyl)benzene in the first stage of this reaction sequence. [2]

Mass of bromine = ... g

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

....

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

....

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END OF PAPER

Question number	Additional page, if required. Write the question number(s) in the left-hand margin.

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