Surname	StemUp Model Solution	Centre Number	Candidate Number
First name(s)			2

GCE A LEVEL

A410U20-1

Z22-A410U20-1

MONDAY, 20 JUNE 2022 – MORNING

CHEMISTRY – A level component 2

Organic Chemistry and Analysis

2 hours 30 minutes

For Examiner's use only		
Question	**Maximum Mark**	**Mark Awarded**
1. to 4.	**15**	
5.	**16**	
6.	**16**	
7.	**15**	
8.	**18**	
9.	**20**	
10.	**20**	
Total	**120**	

Section A
Section B

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01

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.

You may use a pencil for graphs and diagrams only.

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

Section A Answer **all** questions.
Section B Answer **all** questions.

Write your answers in the spaces provided in this booklet. 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.

Candidates are advised to allocate their time appropriately between **Section A (15 marks)** and **Section B (105 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 120.

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.8**(e) and **Q.10**(b)(ii).

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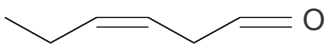
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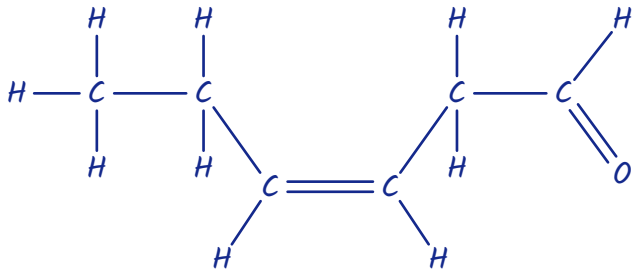
SECTION A

Answer **all** questions.

1. The smell of freshly cut grass is partly due to (*Z*)-hex-3-enal.



(a) Give the **displayed** formula of this compound. [1]



(b) (*Z*)-hex-3-enal and cyclopentanal have the same molecular formula.

(i) Calculate the percentage of oxygen by mass in these compounds. Give your answer to **three** significant figures. [2]

$M_r\ (C_6H_{10}O) = (6 \times 12.0) + (10 \times 1.01) + 16.0 = 98.1$

% oxygen $= (16.0 \div 98.1) \times 100 = 16.3$

Percentage by mass = 16.3 %

(ii) State a chemical test that will give a positive result for (*Z*)-hex-3-enal but not for cyclopentanal. Give the result of the test. [1]

Add aqueous bromine (bromine water) to each: (Z)-hex-3-enal decolourises it (orange to colourless); cyclopentanal does not.

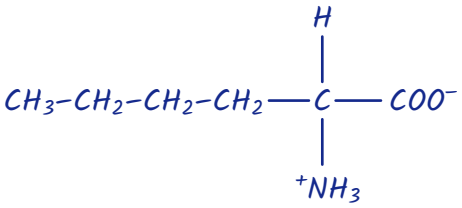
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2. (a) At a certain pH the amino acid norleucine, $CH_3(CH_2)_3CH(NH_2)COOH$, exists as its zwitterion form.

Draw the structure of this zwitterion. [1]



(b) A student was provided with a solution containing a mixture of the amino acids norleucine and isoleucine.

He obtained a thin layer chromatogram of the mixture but found that both norleucine and isoleucine had the same R_f value, using a particular solvent.

Suggest how he might obtain a thin layer chromatogram where these two amino acids have different R_f values. [1]

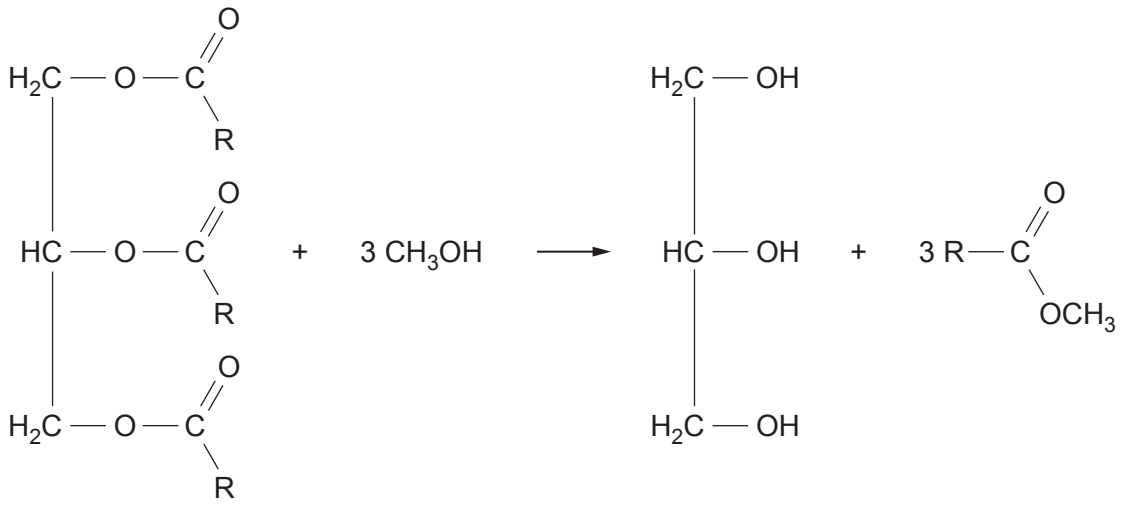
Run it again with a different solvent (or run a two-way chromatogram).

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3. Biodiesel is an increasingly important fuel that is made from fats and oils. This fuel is often the methyl ester of a long chain fatty acid, produced by reacting the starting fat or oil with methanol.



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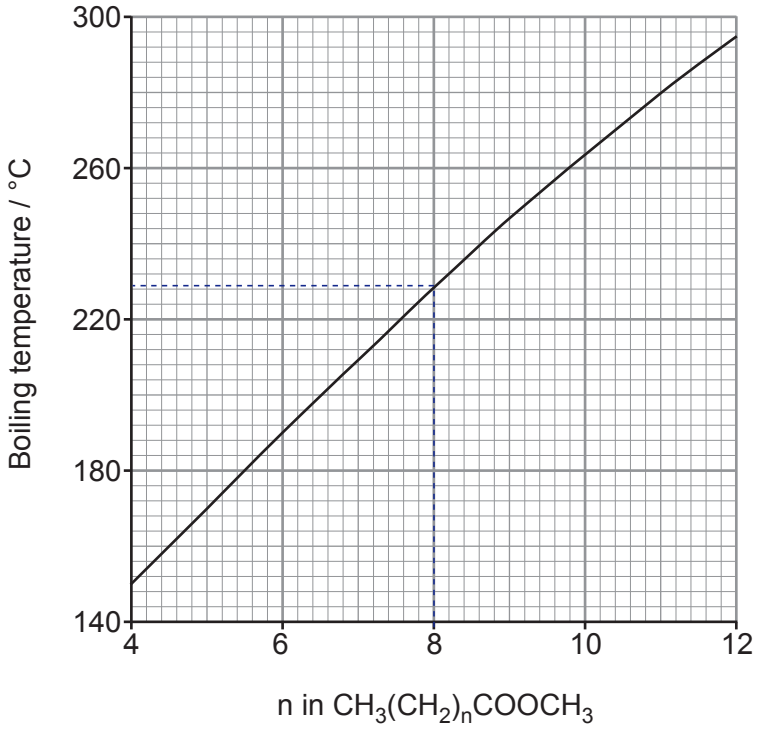
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(a) The alkyl group in this ester is generally a linear chain of between 9 and 18 carbon atoms, depending on the source of the fat or oil.

The boiling temperature of these methyl esters increases as the length of the carbon chain increases.

Use the graph to deduce the boiling temperature of methyl decanoate, $C_{11}H_{22}O_2$. [1]



Boiling temperature ..... 230 ..... °C

(b) Comment on how the shape of the graph supports the statement that 'as the length of the alkyl chain increases, the relative effect of the polar group on the boiling temperature becomes less important'. [1]

It is a curve, not a straight line: each extra CH_2 raises the boiling temperature by less and less. If the polar group's effect were a constant factor the graph would be a straight line.

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(c) One problem with producing methyl esters for use as biofuels is the co-product, propane-1,2,3-triol, for which there is a limited market.

One use for this triol is in the manufacture of epichlorohydrin (C_3H_5ClO) [M_r 92.6].

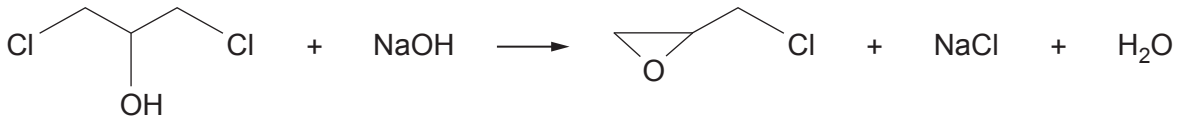
This is made from propane-1,2,3-triol in a two-stage process.

Stage 1



propane-1,2,3-triol
M_r 92.1

Stage 2



epichlorohydrin

Calculate the atom economy of this two-stage reaction.

You should only consider propane-1,2,3-triol, hydrogen chloride and sodium hydroxide as reactants and epichlorohydrin as the required product in your calculation. [1]

Atom economy = M_r of epichlorohydrin ÷ total M_r of reactants × 100

= 92.6 ÷ (92.1 + [2 × 36.5] + 40.0) × 100

= 92.6 ÷ 205.1 × 100 = 45.1

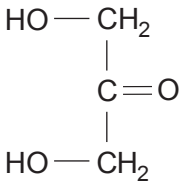
Atom economy = ... 45.1 ..... %

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(d) Another product made from propane-1,2,3-triol is 1,3-dihydroxypropanone.



(i) The traditional method of manufacture is via a biochemical route using propane-1,2,3-triol and appropriate bacteria.

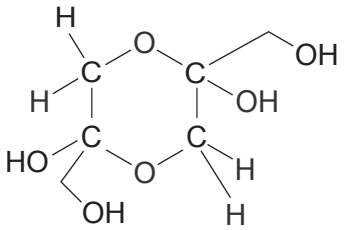
A more modern method uses the aerial oxidation of this triol, in the presence of a catalyst.

Suggest **two** factors, apart from cost, that should be considered when choosing which of these two methods should be used. [2]

1. *The yield of 1,3-dihydroxypropanone obtained by each method.*

2. *The energy (temperature) needed, and the rate of reaction.*

(ii) 1,3-Dihydroxypropanone generally occurs as its dimer, from which the monomer is obtained by dissolving it in water.



Identify a bond that is present in the monomer which is absent in the dimer, suggesting an infrared absorption value for this bond. [1]

C=O bond (ketone), absorbing at about 1700 cm^{-1} (1650 to 1750).

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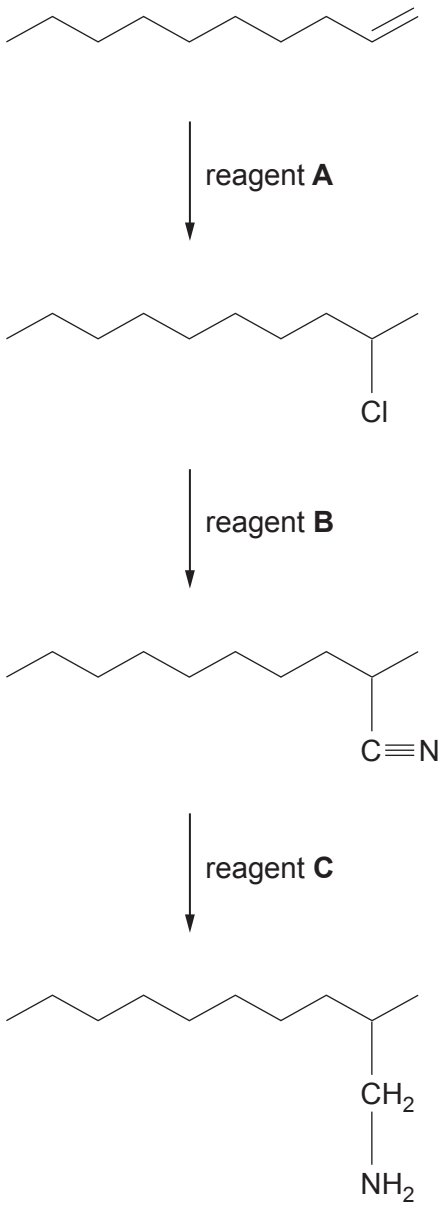
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4. The sequence below shows a method for producing 2-methyldecylamine from dec-1-ene.

State the reagent used in each of the three stages. [3]



Reagent **A** HCl (hydrogen chloride)

Reagent **B** KCN (potassium cyanide)

Reagent **C** $LiAlH_4$ (lithium tetrahydridoaluminate(III))

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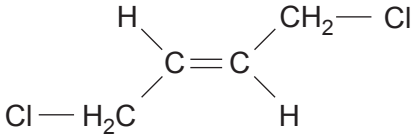
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SECTION B

Answer **all** questions.

5. (a) 1,4-Dichlorobut-2-ene is an important intermediate in the production of the synthetic rubber Neoprene. It exists as (*E*) and (*Z*) isomers.



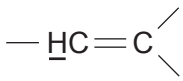
(E)-1,4-dichlorobut-2-ene

(i) Explain why 1,4-dichlorobut-2-ene exists as (*E*) and (*Z*) isomers. [2]

Each carbon atom of the C=C double bond has two different groups attached to it (H and CH_2Cl).

There is no free rotation about the C=C double bond, so the CH_2Cl groups can be on the same side (Z) or opposite sides (E).

(ii) Describe the ^{1}H NMR spectrum of 1,4-dichlorobut-2-ene by completing the table. [2]

Group	Chemical shift δ / ppm	Splitting pattern
$ClC\underline{H}_2$	*3.1 to 4.3*	*doublet*
	*4.5 to 6.3*	*triplet*

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(iii) The mass spectrum of 1,4-dichlorobut-2-ene shows a strong fragmentation signal at m/z 75.

The two common isotopes of chlorine are ^{35}Cl and ^{37}Cl in the ratio of 3:1.

Suggest a formula for this fragmentation signal at m/z 75. Show your working. [2]

$ClCH_2$ = 49 (with ^{35}Cl) or 51 (with ^{37}Cl)

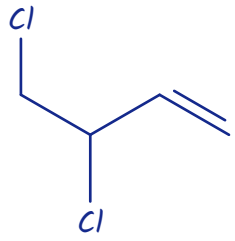
CH=CH = 26, so 49 + 26 = 75

M^+ loses CH_2Cl, leaving the fragment with ^{35}Cl:

$[CH_2{}^{35}Cl–CH=CH]^+$

(iv) I. 1,4-Dichlorobut-2-ene is made from butadiene by chlorination. This then undergoes a rearrangement to give 3,4-dichlorobut-1-ene.

Give the **skeletal** formula of 3,4-dichlorobut-1-ene. [1]



II. 3,4-Dichlorobut-1-ene is then further reacted to give 2-chlorobuta-1,3-diene, $H_2C=C(Cl)-CH=CH_2$.

Suggest a reagent that can be used for this stage. [1]

NaOH in ethanol (alcoholic NaOH), heat

III. Radical polymerisation of 2-chlorobuta-1,3-diene (chloroprene) gives the medically important material poly(chloroprene) or Neoprene.

This polymer has important uses in gloves and facemasks that help to prevent transmission of the Covid-19 virus.

State what is meant by the term 'radical' and give the formula of a radical of your own choice. [2]

An atom or molecule with an unpaired electron, e.g. Cl· (or $\cdot CH_3$).

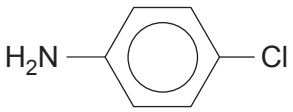
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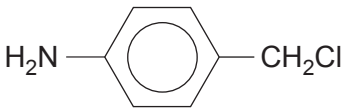
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(b) (i) Explain why 4-chlorophenylamine does not react readily with aqueous sodium hydroxide but (4-chloromethyl)phenylamine produces (4-hydroxymethyl)phenylamine when treated with the same reagent.



4-chlorophenylamine



(4-chloromethyl)phenylamine

You should refer to both compounds in your answer. [2]

(4-Chloromethyl)phenylamine: the Cl is on an aliphatic CH_2 carbon; the C–Cl bond is polarised $C^{\delta+}–Cl^{\delta-}$, so OH^- (nucleophile) attacks the δ+ carbon: nucleophilic substitution.

4-Chlorophenylamine: the Cl is bonded to the ring; a Cl lone pair is delocalised into the ring, so this aryl C–Cl bond is stronger than an alkyl C–Cl bond and no substitution occurs.

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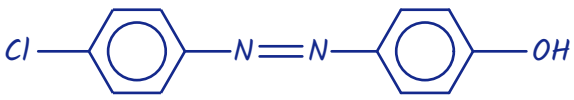
(ii) 4-Chlorophenylamine reacts with nitric(III) acid (produced from sodium nitrate(III) and hydrochloric acid) to give a diazonium compound.

This can then react with phenol to give an azo dye.

I. State the temperature necessary to produce a diazonium compound. [1]

5 to 10 °C

II. Give the structure of the azo dye produced in this reaction. [1]



III. Another azo dye, Solvent Yellow 7, has a maximum absorption in its UV-visible spectrum at a wavelength of 347 nm.

Calculate the frequency of this maximum absorption. [2]

$c = f\lambda$, so $f = c \div \lambda$

$f = 3.00 \times 10^{8} \div (347 \times 10^{-9})$

$f = 8.65 \times 10^{14}$ Hz

Frequency = 8.65×10^{14} Hz

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6. (a) (i) Benzamide reacts with aqueous sodium hydroxide to produce sodium benzoate and ammonia.



6.30 g of a damp solid sample of benzamide reacted with an excess of aqueous sodium hydroxide to give 0.0500 mol of ammonia.

Calculate the percentage purity of this sample of benzamide. [2]

1 mol benzamide gives 1 mol NH_3, so 0.0500 mol benzamide

M_r benzamide (C_7H_7NO) = 121

mass of pure benzamide = 0.0500 × 121 = 6.05 g

purity = 6.05 ÷ 6.30 × 100 = 96.0%

Purity = *96.0* %

(ii) Benzamide starts to decompose at 100 °C into benzonitrile and water.

Suggest how this damp sample should be treated to give a dry sample. [1]

Dry it at a temperature below 100 °C (e.g. in a warm oven at 60 °C), or leave it in a desiccator.

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(b) (i) The addition of a solute to a solvent gives a solution that has a lower freezing temperature than the pure solvent. The freezing temperature obtained can be used to find the relative molecular mass of the solute.

In a modification to this method 0.698 g of a substituted amide, **R**–CONH(C_6H_5), was mixed with 5.00 g of camphor and the freezing temperature of the mixture found.

Pure camphor freezes at 179 °C and the freezing temperature of the mixture was 145 °C.

Use the formula below to work out the relative molecular mass (M_r) of the amide. [1]

$$\Delta T = \frac{1000 \times w \times k}{W \times M_r}$$

where ΔT is the lowering of the freezing temperature
w is the mass of the substituted amide
W is the mass of camphor
k is 39.7

$\Delta T = 179 - 145 = 34\ °C$

$M_r = (1000 \times w \times k) \div (W \times \Delta T)$

$M_r = (1000 \times 0.698 \times 39.7) \div (5.00 \times 34) = 163$

$M_r =$ 163

(ii) Use the answer to part (i) to show that 'M_r' for the **R** group is 43. [1]

'M_r' of R = 163 − M_r of $CONH(C_6H_5)$

= 163 − (12.0 + 16.0 + 14.0 + 1.0 + 72.0 + 5.0)

= 163 − 120 = 43

(iii) **R** represents the formula of a saturated hydrocarbon chain.

Deduce a molecular formula for the **R** group. [1]

R is C_3H_7

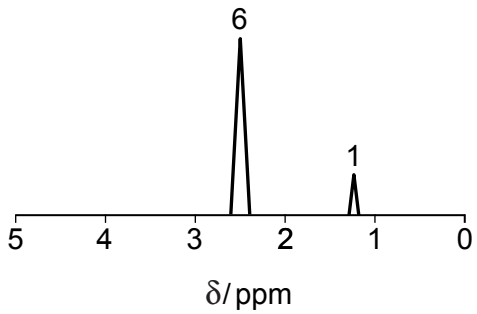
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(iv) The diagram shows the low resolution ^{1}H NMR spectrum of the **R** group.



Use the spectrum to deduce the structure of the **R** group. Explain your answer. [2]

R is $(CH_3)_2CH-$, the propan-2-yl (isopropyl) group.

There are only two proton environments, with peak areas in the ratio

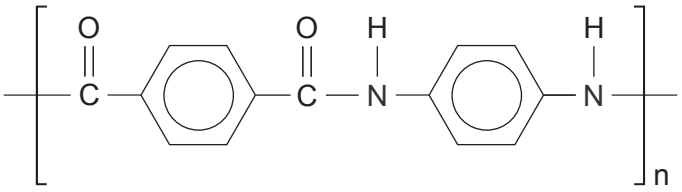
6:1: six equivalent protons (two CH_3) and one CH proton.

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(c) The structure of the repeating unit of the condensation polymer Nomex© is shown below.



One way of producing this polymer is from benzene-1,3-dicarbonyl dichloride and benzene-1,3-diamine.

(i) Give the **empirical** formula of benzene-1,3-diamine. [1]

C_3H_4N

(ii) Nomex© is formed by condensation polymerisation.

State the meaning of 'condensation polymerisation'. [1]

Monomers join together with the elimination of a small molecule (such as HCl or H_2O) at each link.

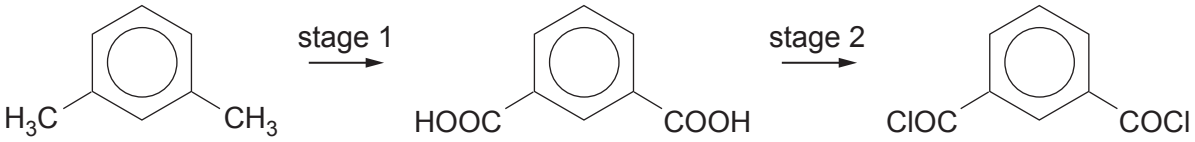
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(iii) Benzene-1,3-dicarbonyl dichloride is produced from 1,3-dimethylbenzene.



I. State a reagent that can be used in the laboratory for stage 1. [1]

alkaline $KMnO_4$ (potassium manganate(VII)), heat

II. State a reagent that can be used in the laboratory for stage 2. [1]

$SOCl_2$ (thionyl chloride)

(iv) Polyamides such as Nomex© are very slowly decomposed by heating with aqueous sodium hydroxide.

Suggest how the rate of this slow reaction can be increased. [1]

Heat it to a higher temperature (e.g. reflux), or use a more concentrated NaOH solution.

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(d) Urea, $CO(NH_2)_2$, has an important use in reducing atmospheric pollution by reacting with nitrogen oxides in diesel exhaust fumes.

$$4CO(NH_2)_2 + 6NO_2 \longrightarrow 7N_2 + 8H_2O + 4CO_2$$

M_r 60 M_r 46

For this purpose, it is supplied as an aqueous solution containing 480 g dm^{-3} of urea.

(i) Calculate the mass of nitrogen(IV) oxide that can be removed from diesel exhaust fumes by 5 dm^3 of the urea solution. Give your answer in kg. [2]

moles of urea = (5 × 480) ÷ 60 = 40 mol

moles of NO_2 = 40 × 6/4 = 60 mol

mass of NO_2 = 60 × 46 = 2760 g = 2.76 kg

Mass = 2.76 kg

(ii) This reaction removes toxic nitrogen(IV) oxide from the exhaust fumes.

Use the equation to suggest **one** disadvantage of this reaction. Explain your answer. [1]

CO_2 is produced, which is a greenhouse gas and contributes to global warming.

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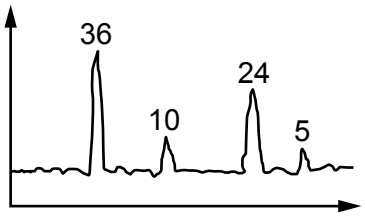
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7. (a) In many parts of the world biting insects are major carriers of disease and a number of natural products and synthetic compounds have been used to combat this threat.

One of the natural products that has been used is citronella oil, obtained from the lemongrass plant.

(i) The chromatogram shows some of the components of this oil. The figures indicate the proportion of each compound present by volume. The major component of the oil is citronellal.

Calculate the percentage of citronellal in this sample of citronella oil. [1]



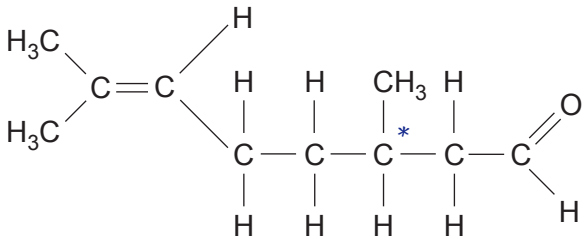
total = 36 + 10 + 24 + 5 = 75

% citronellal = 36 ÷ 75 × 100 = 48

Percentage = ... *48* ..... %

(ii) The formula of citronellal is shown below.

Indicate any chiral centres shown in this formula by using an asterisk (*). [1]



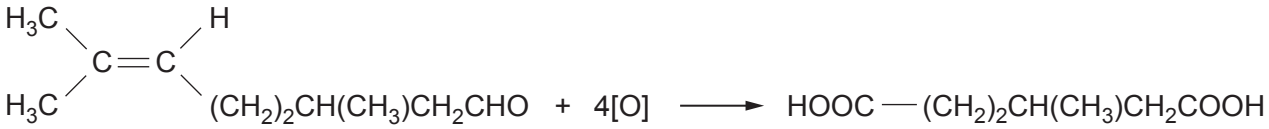
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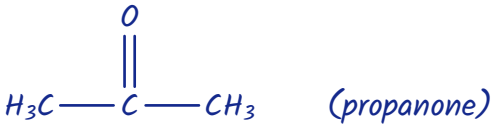
(iii) Citronellal can be oxidised to 3-methylhexane-1,6-dioic acid and compound **E**.

Use the equation to find the molecular formula for compound **E** and then suggest its possible structure. [2]



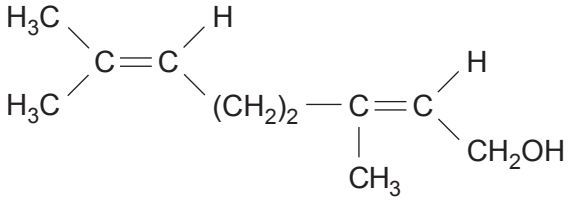
citronellal = $C_{10}H_{18}O$; acid = $C_7H_{12}O_4$

E = $C_{10}H_{18}O + 4[O] - C_7H_{12}O_4 = C_3H_6O$



(propanone)

(iv) Citronella oil also contains geraniol.



The structure of geraniol shows that it contains two double bonds between carbon atoms.

Calculate the volume of bromine that will need to be added to just react with 0.020 mol of geraniol.

The density of bromine is 3.2 g cm^{-3}. [2]

1 mol geraniol reacts with 2 mol Br_2 (two C=C)

moles Br_2 = 2 × 0.020 = 0.040 mol

mass Br_2 = 0.040 × 159.8 = 6.39 g

volume = 6.39 ÷ 3.2 = 2.0 cm^3

Volume = ... *2.0* ..... cm^3

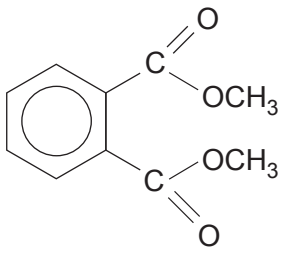
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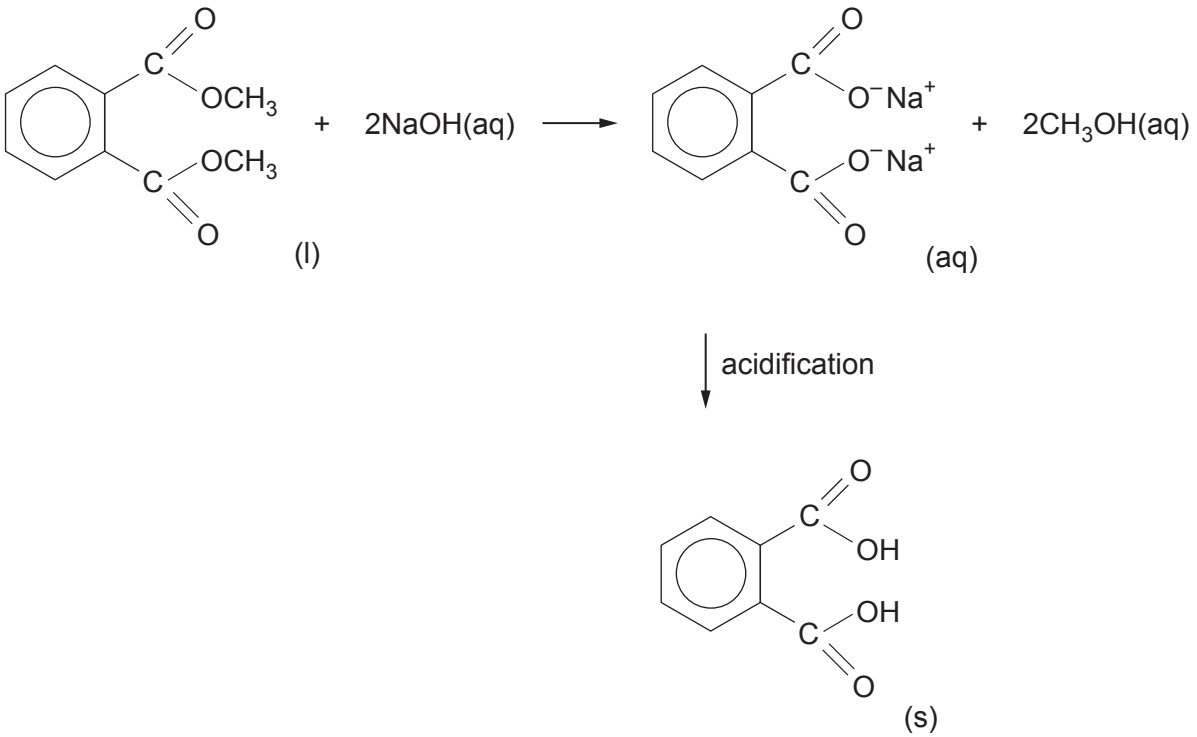
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(b) Dimethyl benzene-1,2-dicarboxylate (DMP) is a liquid ester that has also been used to repel insects.



DMP can be hydrolysed to benzene-1,2-dicarboxylic acid by refluxing it with aqueous sodium hydroxide, followed by acidification.



(i) Describe what is meant by the term 'refluxing'. [1]

Heating the mixture so it boils at a constant temperature with a vertical condenser fitted, so vapours condense and drip back into the flask without loss of material.

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(ii) DMP and aqueous sodium hydroxide are immiscible.

Use the equation to deduce what will be observed when the refluxing stage has gone to completion. [1]

The two layers disappear: only one (aqueous) layer remains, as all the products are soluble in water.

(iii) After refluxing, the mixture is acidified and the solid benzene-1,2-dicarboxylic acid is filtered off. It is then recrystallised from water.

State what should be done to the filtered solid before it is recrystallised. [1]

Wash it with a little cold water to remove traces of soluble impurities (e.g. NaCl).

(iv) The solubility of benzene-1,2-dicarboxylic acid in water at two temperatures is shown in the table.

Temperature / °C	Solubility / g per 100 g H_2O
14	0.7
100	18.0

Calculate the mass of acid precipitated if a solution containing 8.0 g of the acid in 50 g of water is cooled from 100 °C to 14 °C. [1]

at 14 °C: 0.7 g per 100 g water, so 0.35 g stays dissolved in 50 g

mass precipitated = 8.0 − 0.35 = 7.65 g

Mass = 7.65 g

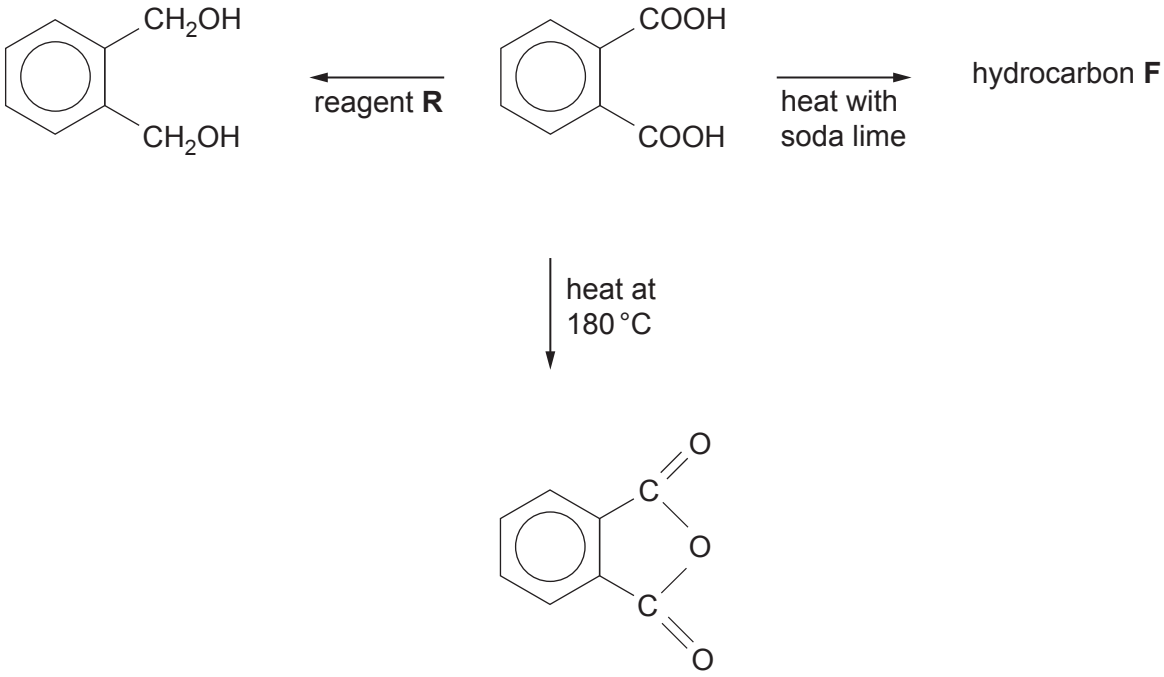
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(c) Some of the reactions of benzene-1,2-dicarboxylic acid are shown below.

Use this flow chart to answer the questions that follow.



(i) Give the **formula** of reagent **R**. [1]

LiAlH$_4$

(ii) Give the structure of hydrocarbon **F**. [1]



(iii) State the type of reaction that occurs when benzene-1,2-dicarboxylic acid is heated at 180 °C. [1]

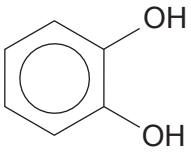
dehydration (elimination of water)

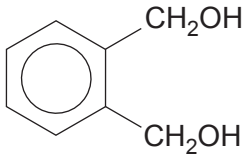
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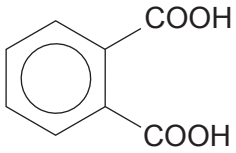
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(d) Describe a chemical test that will identify which of these three compounds, present in separate unlabelled aqueous solutions, is the most acidic. [2]







Add $NaHCO_3(aq)$ to each: effervescence (CO_2 gas) is seen only with the most acidic compound, the dicarboxylic acid.

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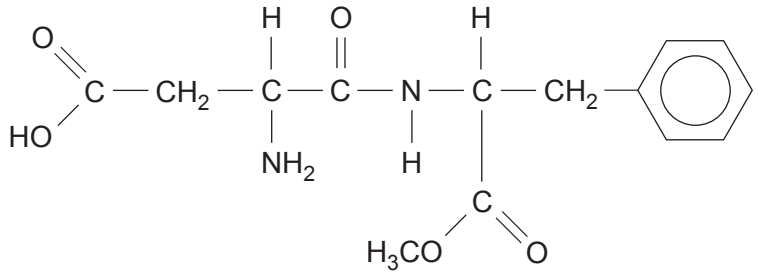
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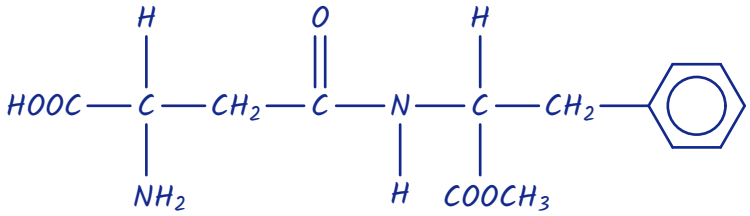
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8. (a) Aspartame is a dipeptide produced from aspartic acid and the methyl ester of phenylalanine.

The structure of α-aspartame is shown, where one COOH group of aspartic acid bonds to the NH_2 group of the methyl ester of phenylalanine.



Write the structure of β-aspartame, in which the other COOH group of aspartic acid bonds to the NH_2 group. [1]



(b) Both α- and β-aspartame (M_r 294) react with aqueous sodium hydroxide. In this reaction 3 mol of sodium hydroxide react with 1 mol of aspartame.

Calculate the volume of aqueous sodium hydroxide of concentration 4.00 mol dm^{-3} needed to just react with 73.5 g of aspartame. [2]

moles of aspartame = 73.5 ÷ 294 = 0.250 mol

moles of NaOH = 3 × 0.250 = 0.750 mol

volume = 0.750 ÷ 4.00 = 0.1875 dm^3 = 187.5 cm^3

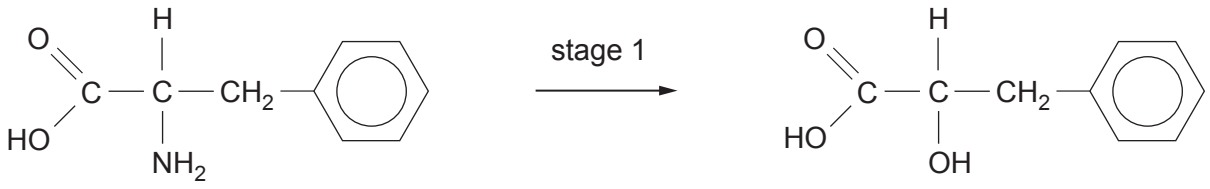
Volume = 187.5 cm^3

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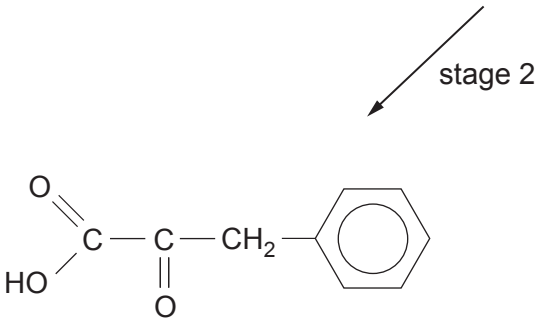
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(c) Phenylalanine can be converted to compound **T** in a two-stage reaction.



compound **S**



compound **T**

(i) Suggest a reagent(s) that can be used in stage 1 to produce compound **S**. [1]

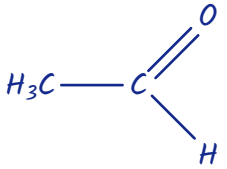
HNO_2 (from $NaNO_2$ and HCl(aq))

(ii) Explain why stage 2 can be described as an oxidation reaction. [1]

Hydrogen is removed: the CH(OH) group loses two H atoms to become C=O.

(iii) Unusually, compound **T** reacts with Tollens' reagent to give a silver mirror.

Give the structure of any other compound that will also produce a silver mirror with Tollens' reagent. [1]



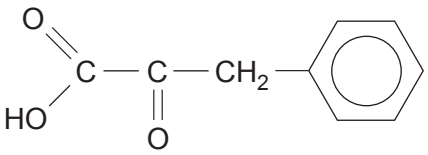
(ethanal, CH_3CHO)

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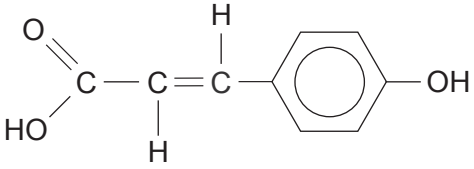
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(d) Compound **T** and compound **U** are isomers of formula $C_9H_8O_3$.



compound **T**



compound **U**

(i) State the name of an element that will produce effervescence when added to a solution of either of these two compounds. [1]

magnesium

(ii) State what is seen when aqueous iron(III) chloride is added to a solution of compound **U**. [1]

a purple colour forms

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(iii) Compound **U** reacts with aqueous bromine to give compound **V**.

Each molecule of compound **V** contains 9 carbon atoms and 3 oxygen atoms, as well as hydrogen and bromine.

Its mass spectrum shows a molecular ion at m/z 482.

Use this information to deduce a possible structure for compound **V**. Show your reasoning. [4]

M_r of V = 482

9 C + 3 O = (9 × 12.0) + (3 × 16.0) = 108 + 48 = 156

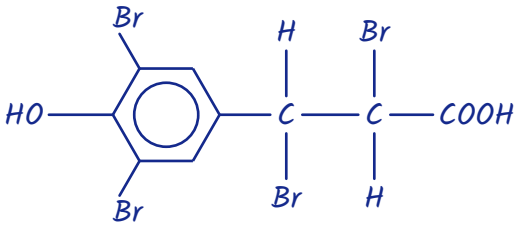
482 − 156 = 326 left for H and Br

4 Br = 4 × 79.9 = 319.6; 326 − 319.6 = 6.4, so 6 H

V is $C_9H_6Br_4O_3$ (U = $C_9H_8O_3$):

Br_2 adds across the C=C (2 Br) and 2 Br substitute

into the phenol ring at the 2- and 6-positions to the OH.



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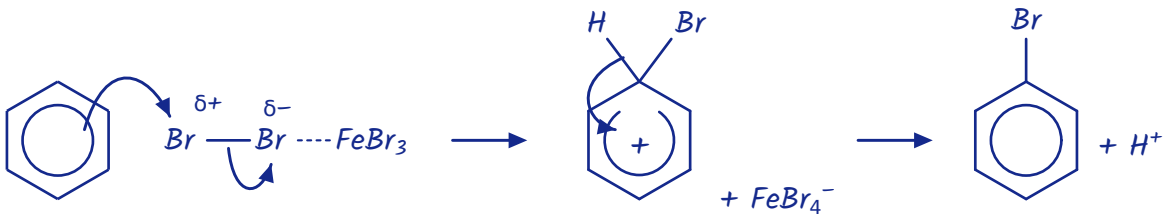
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(e) Many characteristic reactions of benzene involve electrophilic substitution.

Discuss this statement, illustrating your answer by the bromination of benzene.

Your answer should include the mechanism for this reaction and any necessary conditions. [6 QER]

$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$ (*$FeBr_3$ polarises Br–Br*)



$H^+ + FeBr_4^- \rightarrow HBr + FeBr_3$ (*catalyst regenerated*)

Benzene is planar; a p orbital on each C overlaps to give a delocalised π electron cloud above and below the ring, giving extra stability. This high electron density attracts electrophiles.

Addition would destroy the delocalisation, so benzene undergoes substitution: H is replaced by Br, the delocalised ring is restored and stability is retained.

Conditions: Br_2 with $FeBr_3$ catalyst (halogen carrier), room temperature, dry.

$FeBr_3$ polarises Br_2 ($Br^{\delta+}$–$Br^{\delta-}$) giving the electrophile Br^+.

Br^+ accepts a π electron pair, forming a C–Br bond and a positive intermediate; the C–H bond breaks and its electrons restore the ring, giving bromobenzene and H^+; $H^+ + FeBr_4^-$ regenerates $FeBr_3$.

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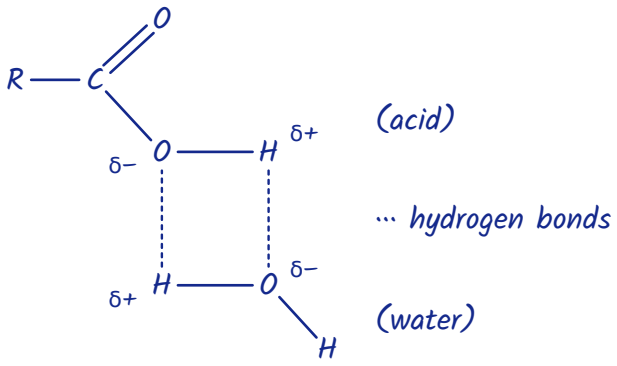
9. (a) The solubilities of some straight chain aliphatic carboxylic acids, **R**–COOH, in water at 20 °C are shown in the table.

Number of carbon atoms in the **R** group	Solubility / g per 100 g H_2O
4	5.00
5	1.10
6	0.50
7	0.07
8	0.03

(i) State the name of the carboxylic acid that has 7 carbon atoms in its **R** group. [1]

octanoic acid

(ii) Explain why the solubility decreases as the number of carbon atoms in the **R** group increases. Include a suitable diagram in your answer. [3]



The solubility depends on the polar COOH group forming hydrogen bonds with water molecules.

As R gets longer the COOH group forms an increasingly small part of the molecule; the non-polar chain cannot hydrogen bond, and the extra van der Waals forces are weaker than the hydrogen bonds lost, so solubility decreases.

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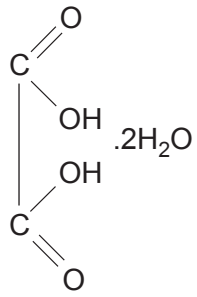
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(b) Ethanedioic acid was first made in 1776 by oxidising sucrose with concentrated nitric acid (represented as [O] in the equation below).

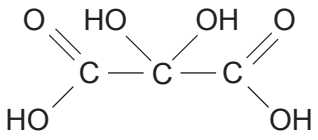
(i) Complete the equation for this reaction. [1]

$C_{12}H_{22}O_{11}$ + 18 [O] ⟶ 6 $(COOH)_2$ + 5 H_2O

(ii) Ethanedioic acid is obtained from the aqueous mixture as the dihydrate.
A small quantity of hydrated mesoxalic acid is also formed during this reaction.



ethanedioic acid dihydrate



hydrated mesoxalic acid

I. If the ethanedioic acid dihydrate is contaminated with a small quantity of hydrated mesoxalic acid, describe how the melting temperature of the dihydrate will be affected. [1]

It will be lower than for the pure dihydrate, and it will melt over a range of temperature.

II. Explain how the ^{13}C NMR spectra of these hydrated acids would differ.

The position of the signals is **not** required in your answer. [2]

Ethanedioic acid dihydrate gives only one signal, as both carbon atoms are equivalent.

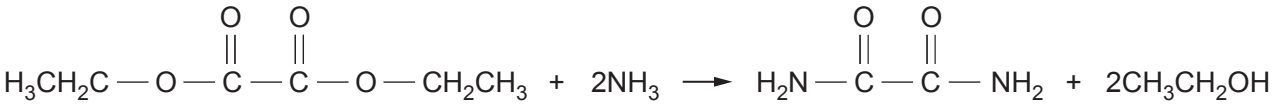
Hydrated mesoxalic acid gives two signals, as it has two different carbon environments (2 × COOH and the central $C(OH)_2$).

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(c) A student made oxamide by reacting diethyl ethanedioate with aqueous ammonia.



oxamide

She followed a book method, starting with 13.5 cm^3 of diethyl ethanedioate.

(i) Calculate the number of moles of diethyl ethanedioate used.

Its density is 1.08 $g\,cm^{-3}$. [2]

mass = 13.5 × 1.08 = 14.6 g

M_r ($C_6H_{10}O_4$) = 146

moles = 14.6 ÷ 146 = 0.100 mol

Number of moles = *0.100* mol

(ii) The method stated that she should obtain a yield of 57%.

Calculate the mass that she should obtain. [1]

M_r oxamide = 88.0; 0.100 mol gives 8.80 g at 100%

mass at 57% = 88.0 × 0.100 × 57 ÷ 100 = 5.02 g

Mass = *5.02* g

(iii) On weighing the product, the student found that she had obtained a yield of 110%.

Apart from incorrect weighing of the product, suggest **two** reasons why this may have happened. [2]

1. *She used more than 13.5 cm^3 of diethyl ethanedioate.*

2. *The product was not dry (still damp/wet).*

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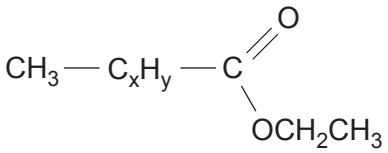
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(d) There is considerable interest in developing drugs that are used to treat high fat levels in the blood.

One compound being studied is E-EPA, which is the ethyl ester of a linear polyunsaturated carboxylic acid, where C_xH_y represents the number of carbon and hydrogen atoms in a long hydrocarbon chain.



(i) 0.0600 mol of E-EPA has a mass of 19.8 g.

Calculate the relative molecular mass (M_r) of E-EPA. [1]

M_r = mass ÷ moles = 19.8 ÷ 0.0600 = 330

M_r = 330

(ii) Use the formula of E-EPA and your answer to part (i) to calculate the 'relative molecular mass' of the C_xH_y part of the molecule. [2]

CH_3 = 15; $COOCH_2CH_3$ = 73

C_xH_y = 330 − (15 + 73) = 242

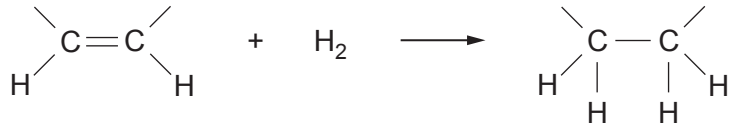
M_r = 242

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(iii) 0.0600 mol of E-EPA reacts with 7.35 dm^3 of hydrogen gas, measured at 298 K and 1 atm, to convert the compound to a saturated ester.



Use this information to find the number of — CH ═ CH — groups present in each molecule of E-EPA. [2]

moles of H_2 = 7.35 ÷ 24.5 = 0.300 mol

ratio = 0.300 ÷ 0.0600 = 5 mol H_2 per mol E-EPA

1 mol H_2 adds to each C=C, so 5 groups

Number of — CH ═ CH — groups = ... 5 .....

(iv) Use your answers to parts (ii) and (iii) to calculate the number of CH_2 groups present in each molecule of E-EPA. [2]

5 –CH=CH– groups = 5 × 26 = 130

242 – 130 = 112

each CH_2 = 14, so 112 ÷ 14 = 8

Number of CH_2 groups = ... 8 .....

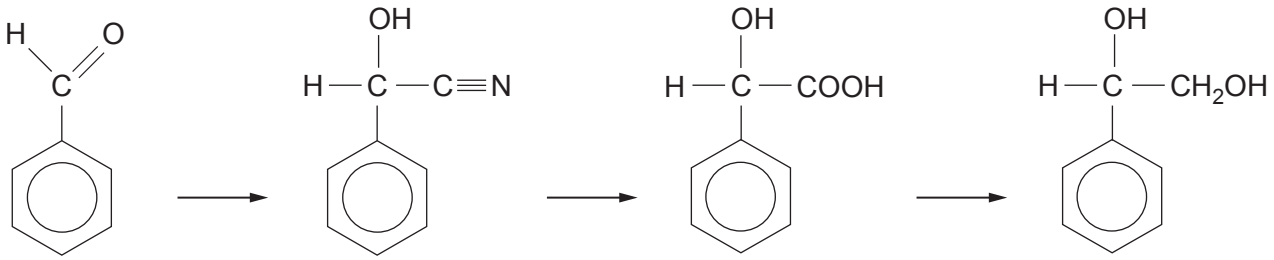
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10. (a) The scheme below shows a sequence of reactions starting from benzaldehyde.

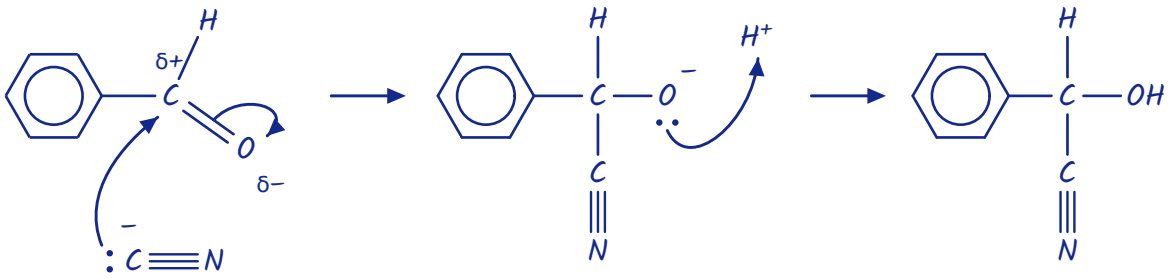


(i) One way of increasing the length of a carbon chain is by reacting an aldehyde with hydrogen cyanide.

I. Show the mechanism for the reaction of benzaldehyde with hydrogen cyanide to produce 2-hydroxy-2-phenylethanenitrile.

Include appropriate charges and curly arrows. [3]

$HCN \rightleftharpoons H^+ + {}^-CN$



II. State the name of the reaction mechanism that you have described in part I. above. [1]

nucleophilic addition

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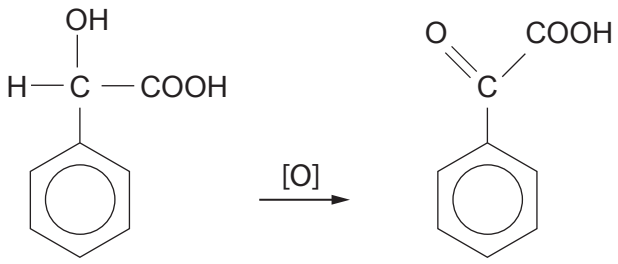
(ii) State a reagent that is used in aqueous solution to convert 2-hydroxy-2-phenylethanenitrile to the corresponding carboxylic acid, 2-hydroxy-2-phenylethanoic acid. [1]

dilute sulfuric acid (or hydrochloric acid), heat

(iii) Suggest why a solution of 2-hydroxy-2-phenylethanoic acid, produced in part (ii), does not show any optical activity when placed in a polarimeter. [1]

The planar C=O can be attacked from either side equally, giving a racemic mixture (equimolar mixture of the two enantiomers).

(iv) 2-Hydroxy-2-phenylethanoic acid can be oxidised to the corresponding keto-acid, compound **W**.



compound **W**

Suggest why compound **W** does not show any optical activity when a solution is placed in a polarimeter. [1]

Compound W has no chiral centre (no asymmetric carbon atom), so it has no optical isomers.

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(v) I. Explain why 2-hydroxy-2-phenylethanoic acid will react with methanol, in the presence of a catalyst.

Give the formula of the organic compound formed. [2]

Ester formed: $C_6H_5CH(OH)COOCH_3$

(methyl 2-hydroxy-2-phenylethanoate)

It contains a COOH group, so it acts as a carboxylic acid and forms an ester with methanol (acid catalyst).

II. Explain why 2-hydroxy-2-phenylethanoic acid can also react with ethanoic acid, in the presence of a catalyst. [1]

It also contains an OH group, so it acts as an alcohol and forms an ester with ethanoic acid.

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(b) Pentan-2-one can be made by the oxidation of pentan-2-ol using acidified potassium dichromate.

(i) State the colour change that is seen in the reaction flask as acidified dichromate is added to pentan-2-ol. [1]

orange to green

(ii) After the reaction the mixture is distilled and the fraction boiling between 100 and 120 °C is collected. This distillate is largely pentan-2-one. It also contains a little unreacted pentan-2-ol and water.

Describe how you would obtain a dry sample of pentan-2-one from this distillate.

It is not necessary to redistil your dry sample of pentan-2-one.

You are given the following information to help you in your answer.

- You should use a separating funnel
- Pentan-2-ol is more soluble than pentan-2-one in water
- Pentan-2-one is very soluble in ethoxyethane
- Ethoxyethane boils at 35 °C and is very flammable
- The density of ethoxyethane is 0.71 g cm^{-3}
- Solid anhydrous magnesium sulfate is a suitable drying agent for pentan-2-one [6 QER]

Pour the distillate into a separating funnel and add water; pentan-2-ol, being more soluble in water than pentan-2-one, dissolves in it.

Add an equal volume of ethoxyethane (dissolves the pentan-2-one); stopper and shake, releasing the pressure often.

Allow to separate: ethoxyethane (0.71 g cm^{-3}) is less dense, so it is the upper layer; run off and discard the lower aqueous layer.

Add anhydrous magnesium sulfate to the ethoxyethane layer and swirl until clear, then filter (or decant) off the solid.

Distil off the ethoxyethane (b.p. 35 °C) using a heating mantle or water bath, no naked flames (very flammable), leaving dry pentan-2-one.

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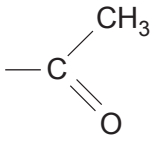
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(iii) Describe how infrared spectroscopy could confirm that there is no longer pentan-2-ol present. [1]

There is no broad O–H absorption at 3200 to 3550 cm^{-1} (alcohol O–H), so no pentan-2-ol is present.

(iv) Give the reagent(s) and an observation to show that pentan-2-one contains the following group. [2]



Warm with iodine and aqueous sodium hydroxide (alkaline iodine): a pale yellow precipitate (CHI_3) forms.

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END OF PAPER

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

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GCE A LEVEL

A410U20-1A

Z22-A410U20-1A

eduqas Part of WJEC

MONDAY, 20 JUNE 2022 – MORNING

CHEMISTRY – A level component 2
Data Booklet

Avogadro constant	N_A	$= 6.02 \times 10^{23}\ \text{mol}^{-1}$
molar gas constant	R	$= 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$
molar gas volume at 273 K and 1 atm	V_m	$= 22.4\ \text{dm}^3\ \text{mol}^{-1}$
molar gas volume at 298 K and 1 atm	V_m	$= 24.5\ \text{dm}^3\ \text{mol}^{-1}$
Planck constant	h	$= 6.63 \times 10^{-34}\ \text{J s}$
speed of light	c	$= 3.00 \times 10^{8}\ \text{m s}^{-1}$
density of water	d	$= 1.00\ \text{g cm}^{-3}$
specific heat capacity of water	c	$= 4.18\ \text{J g}^{-1}\ \text{K}^{-1}$
ionic product of water at 298 K	K_w	$= 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$
fundamental electronic charge	e	$= 1.60 \times 10^{-19}\ \text{C}$

temperature (K) = temperature (°C) + 273

$1\ \text{dm}^3 = 1000\ \text{cm}^3$
$1\ \text{m}^3 = 1000\ \text{dm}^3$
1 tonne = 1000 kg
$1\ \text{atm} = 1.01 \times 10^5\ \text{Pa}$

Multiple	Prefix	Symbol
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

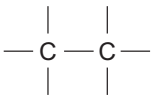
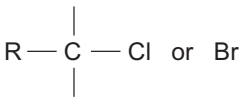
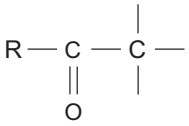
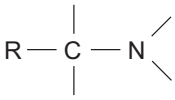
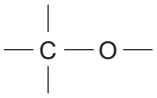
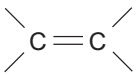
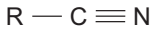
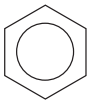
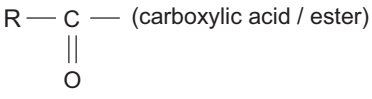
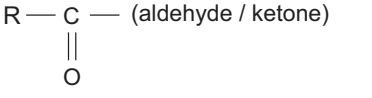
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Infrared absorption values

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 (carboxylic acid)	2500 to 3200 (very broad)
O — H (alcohol / phenol)	3200 to 3550 (broad)
N — H	3300 to 3500

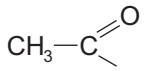
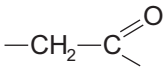
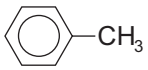
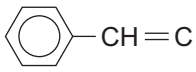
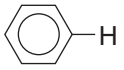
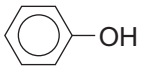
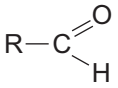
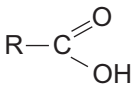
^{13}C NMR chemical shifts relative to TMS = 0

Type of carbon	Chemical shift, δ (ppm)
	5 to 40
	10 to 70
	20 to 50
	25 to 60
	50 to 90
	90 to 150
	110 to 125
	110 to 160
	160 to 185
	190 to 220

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^{1}H NMR chemical shifts relative to TMS = 0

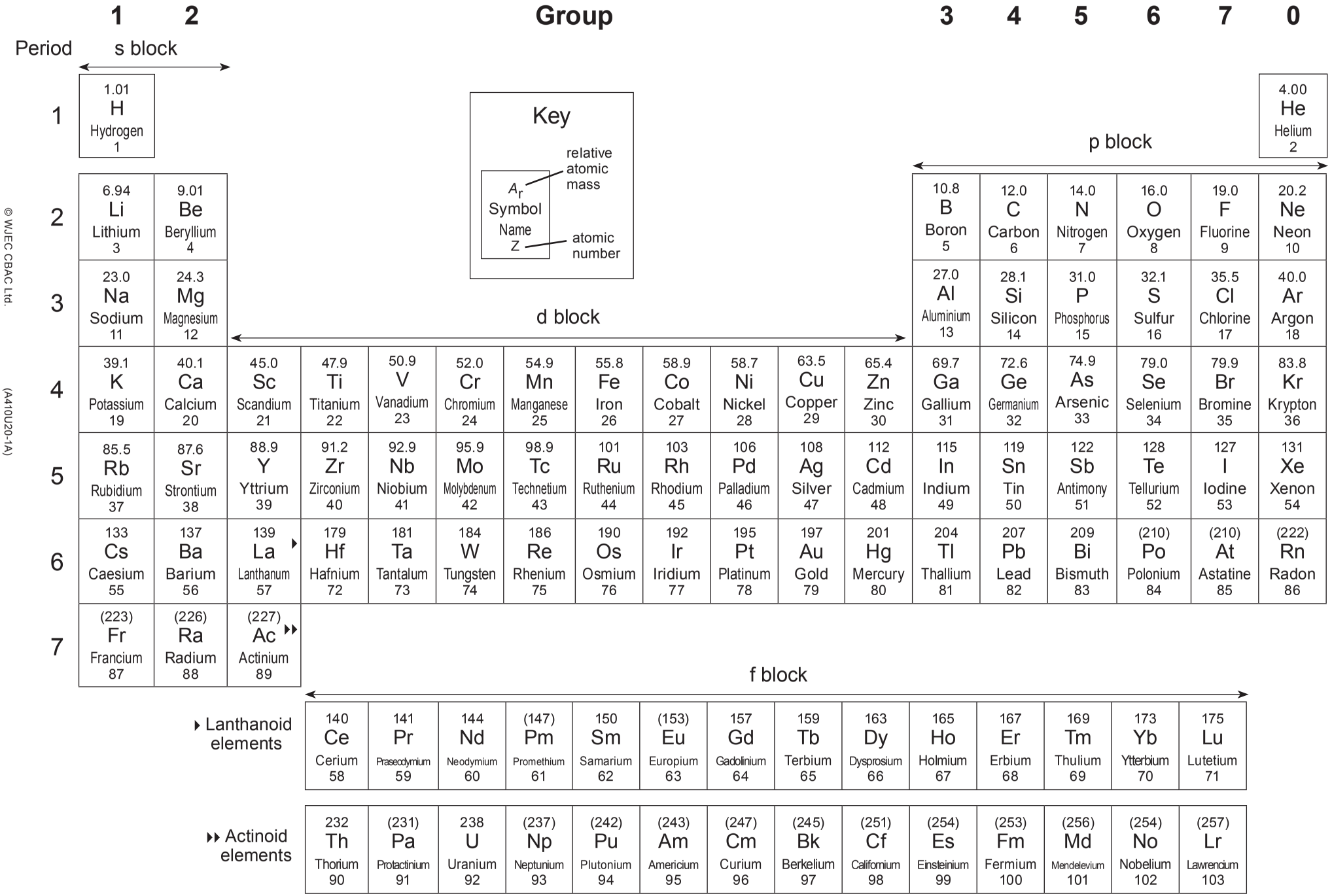
Type of proton	Chemical shift, δ (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
HC—Cl or HC—Br	3.1 to 4.3
HC—O	3.3 to 4.3
R—OH	4.5 *
—C=CH	4.5 to 6.3
—C=CH—CO	5.8 to 6.5
	6.5 to 7.5
	6.5 to 8.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

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THE PERIODIC TABLE



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