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

GCE A LEVEL

A410U20-1

S23-A410U20-1

MONDAY, 19 JUNE 2023 – AFTERNOON

CHEMISTRY – A level component 2

Organic Chemistry and Analysis

2 hours 30 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 9.**	**15**	
Section B	**10.**	**18**	
	11.	**16**	
	12.	**14**	
	13.	**14**	
	14.	**15**	
	15.	**15**	
	16.	**13**	
	Total	**120**	

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ADDITIONAL MATERIALS

- 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.

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 **Q11**(a) and **Q13**(a).

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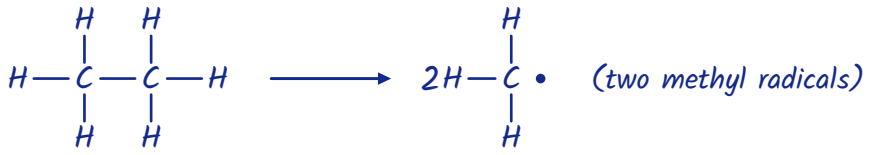
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SECTION A

Answer **all** questions.

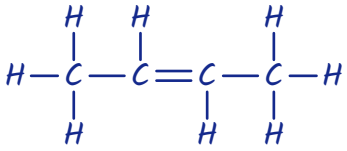
1. Describe what is meant by homolytic bond fission, using ethane as your example. [2]



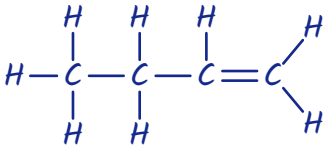
$CH_3–CH_3 \rightarrow CH_3\cdot + \cdot CH_3$

The covalent bond breaks so that each atom in the bond receives one electron from the bonding pair, forming two (free) radicals.

2. Give the formulae of the **two** structural isomers formed when butan-2-ol undergoes dehydration with sulfuric acid. [2]

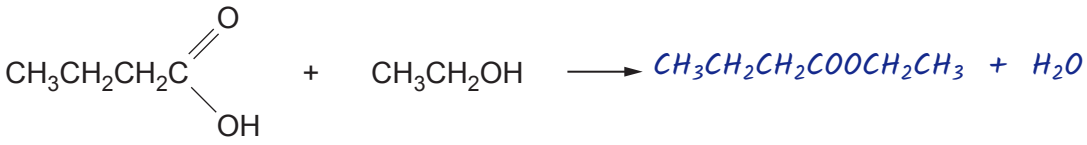


but-2-ene



but-1-ene

3. Complete the equation below and give the name of the organic product. [2]



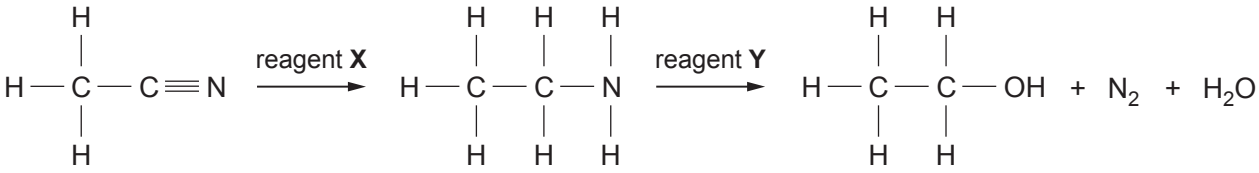
Name ethyl butanoate

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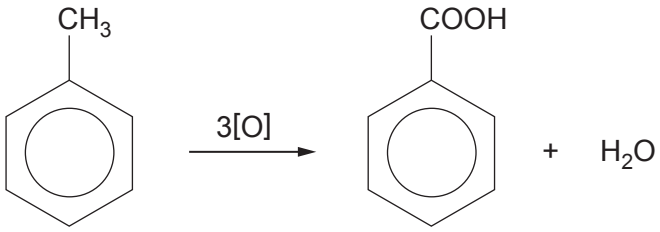
4. Give the reagents **X** and **Y** used in the reaction sequence below. [2]



Reagent **X** *$LiAlH_4$ (lithium tetrahydridoaluminate) in dry ether*

Reagent **Y** *HNO_2 (nitric(III) acid), i.e. $NaNO_2$ and HCl*

5. Benzoic acid can be made by the oxidation of methylbenzene.

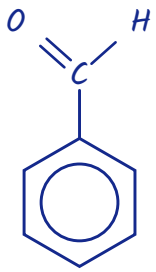


(a) Give a suitable oxidising agent for this reaction. [1]

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

(b) Another product of this oxidation is an organic compound of relative molecular mass 106.

Suggest a structure for this compound. [1]



benzaldehyde, C_6H_5CHO

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6. On strong heating, calcium butanoate produces a ketone and calcium carbonate.

Complete the equation, showing the structure of the ketone. [1]

$(CH_3CH_2CH_2COO)_2Ca \longrightarrow$ $CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$ + $CaCO_3$

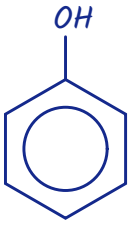
7. The indicator methyl orange is orange/red when seen in white light. Its absorption maximum is at a wavelength of 505 nm.

State the colour seen (if any) when blue-green light of wavelength 505 nm is shone on this material. [1]

no colour seen; black

8. Aqueous iron(III) chloride was added to an organic compound, dissolved in a suitable solvent. The mixture turned to a purple colour.

Suggest a structure for an organic compound which reacts in this way. [1]



phenol, C_6H_5OH

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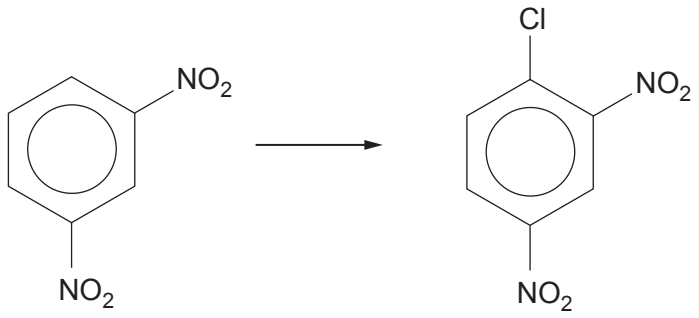
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9. (a) Suggest the reagent(s) needed to carry out the following reaction. [1]



1-chloro-2,4-dinitrobenzene

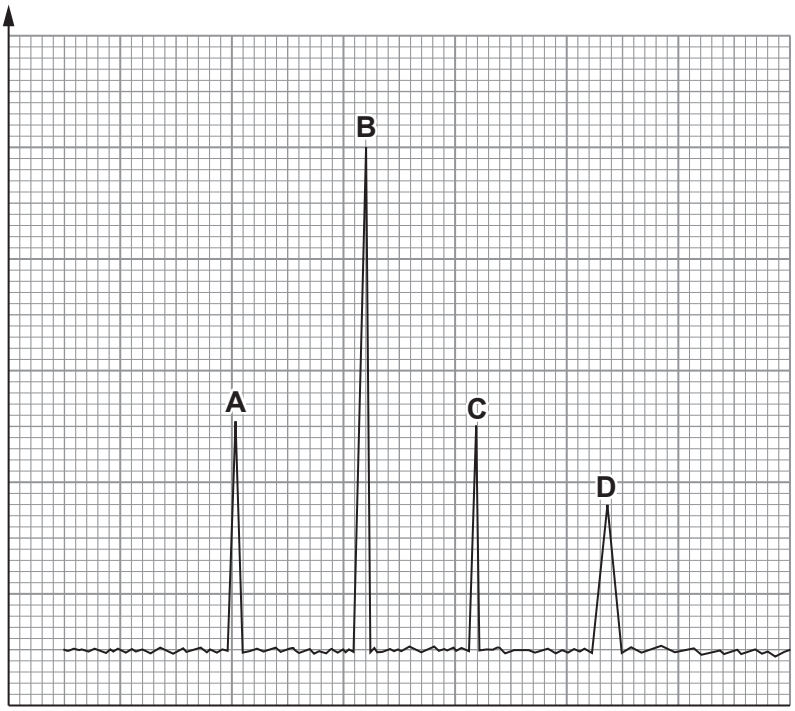
Cl_2 and $AlCl_3$ (or $FeCl_3$) catalyst

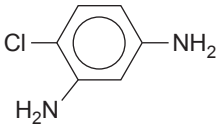
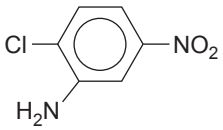
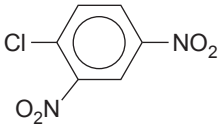
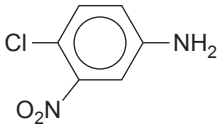
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(b) The diagram shows a gas chromatogram of the products obtained by the reduction of 1-chloro-2,4-dinitrobenzene.



Letter	Compound	Relative peak area	Letter	Compound	Relative peak area
A		32	**C**		31
B		59	**D**		38

Calculate the percentage (by volume) of the fully reduced product, 1-chlorobenzene-2,4-diamine. [1]

percentage = 32 ÷ (32 + 59 + 31 + 38) × 100

= 32 ÷ 160 × 100 = 20%

Percentage = ... *20* ..... %

15

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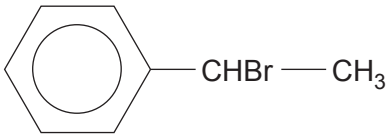
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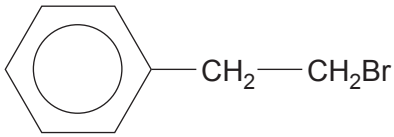
SECTION B

Answer **all** questions.

10. (a) Phenylethene reacts with hydrogen bromide to give largely (1-bromoethyl)benzene, together with smaller quantities of (2-bromoethyl)benzene.



(1-bromoethyl)benzene
boiling temperature 202°C

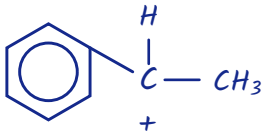


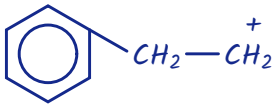
(2-bromoethyl)benzene
boiling temperature 219°C

(i) The reaction of phenylethene with hydrogen bromide is described as electrophilic addition.

Use your knowledge of the addition of hydrogen bromide to propene to explain in detail why (1-bromoethyl)benzene is the major product. [2]

H^+ from HBr adds to a carbon of C=C, via a carbocation intermediate:





secondary carbocation (more stable) *primary carbocation (less stable)*

The secondary carbocation is more stable than the primary one (positive charge stabilised by the electron releasing alkyl group and ring), so it is formed more quickly.

Br^- then attacks this carbocation, hence (1-bromoethyl)benzene is the major product (as with 2-bromopropane from propene).

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(ii) In an experiment 0.082 mol of phenylethene (M_r 104) gave an 85% yield of (1-bromoethyl)benzene (M_r 185).

Calculate the mass of (1-bromoethyl)benzene produced. [2]

moles of product = 0.082 × 85 ÷ 100 = 0.0697 mol

mass = 0.0697 × 185 = 12.9 g

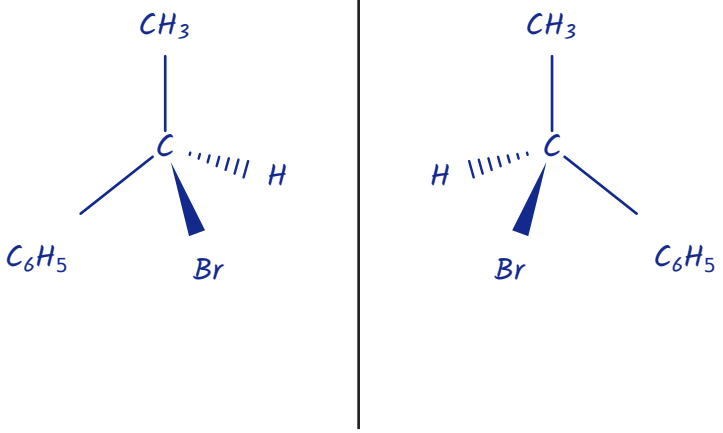
Mass = 12.9 g

(iii) Suggest a method for the separation of these two (bromoethyl)benzenes. [1]

Fractional distillation (boiling temperatures 202 °C and 219 °C).

(iv) (1-Bromoethyl)benzene exists as two enantiomers.

Draw the structures of these two enantiomers. [1]



(v) Explain why (2-bromoethyl)benzene does **not** exist as two enantiomers. [1]

Neither carbon in the side chain is a chiral centre: each has two H atoms, so no carbon has four different groups attached.

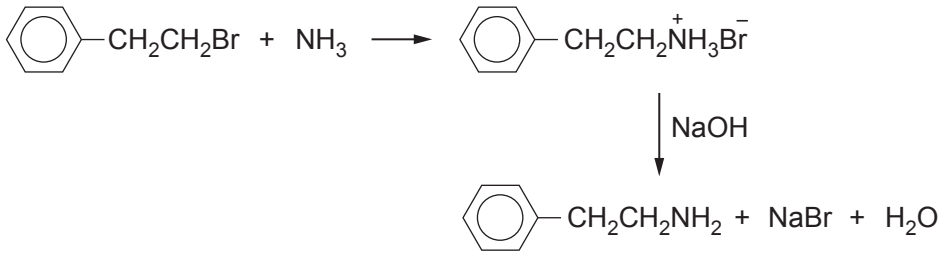
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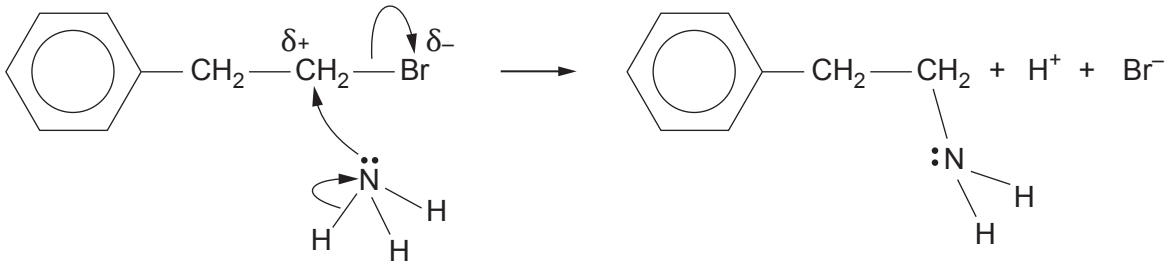
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(b) (2-Bromoethyl)benzene reacts with ammonia.



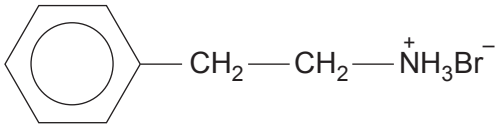
A simplified mechanism for this reaction is shown below.



(i) State the type of reaction mechanism occurring. [1]

nucleophilic substitution

(ii) The initial product of this reaction is the compound whose formula is shown below.



Explain why this salt is formed rather than 2-phenylethylamine and hydrogen bromide. [1]

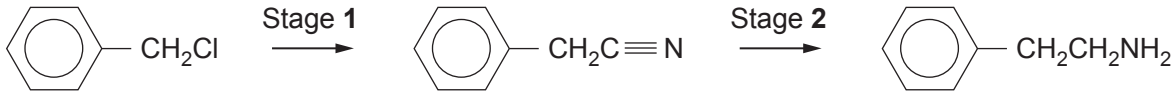
The nitrogen has a lone pair, so it acts as a base: the amine (NH_2) accepts the H^+ (from HBr), forming the ammonium salt.

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(iii) 2-Phenylethylamine can also be produced from (chloromethyl)benzene.



I. State the reagent used in Stage **1**. [1]

KCN (potassium cyanide) in ethanol

II. Use the **Data Booklet** to explain how the infrared absorption value at 2100-2250 cm^{-1} changes during Stage **2**. [1]

The absorption at 2100 to 2250 cm^{-1} decreases (disappears), as the C≡N bond is replaced by a C–N bond.

III. State the type of reaction occurring in Stage **2**. [1]

reduction (addition of hydrogen)

(c) Primary amines, such as 2-phenylethylamine, react with nitric(III) acid to give a quantitative yield of nitrogen gas.



This reaction can be used as a method for finding the percentage purity of a primary amine, by measuring the volume of nitrogen gas produced.

State **three** factors that should be considered when using this method, apart from cost. [3]

1. Temperature (the volume of gas depends on it)
2. Pressure
3. Whether any impurities present also produce nitrogen

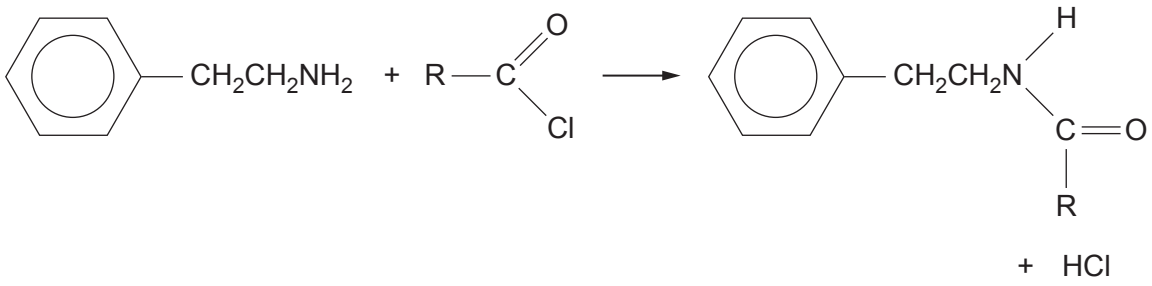
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(d) 2-Phenylethylamine reacts with an acid chloride to give a substituted amide, where R is an alkyl group.



The substituted amide produced contains 7.91% of nitrogen by mass.

Calculate the relative molecular mass of the compound and hence identify R. [3]

$N = 14.0$ is 7.91% of M_r

$M_r = 14.0 \div 7.91 \times 100 = 177$

M_r of $C_6H_5CH_2CH_2NHCO$ fragment = 148

M_r of R = 177 − 148 = 29

so R is CH_3CH_2 (ethyl)

R is CH_3CH_2 (C_2H_5)

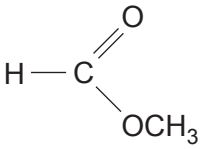
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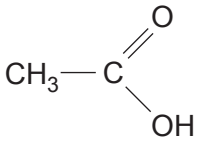
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11. (a) The following compounds are isomers of formula $C_2H_4O_2$.



methyl methanoate boiling temperature 32°C



ethanoic acid boiling temperature 118°C

Compare these compounds referring to their

- reactions with sodium hydrogencarbonate and universal indicator
- relative boiling temperatures
- ^{1}H NMR spectra

In each case you should explain any differences. [6 QER]

Sodium hydrogencarbonate: methyl methanoate is an ester with no acidic H, so no obvious reaction. Ethanoic acid gives effervescence as CO_2 is evolved, showing that it is acidic.

Universal indicator: methyl methanoate stays green, pH 7, as it is neutral (no H^+ or OH^- ions present). Ethanoic acid turns orange, pH below 7 (about 3), as it is a weak acid that partially dissociates, so H^+ ions are present.

Boiling temperature: methyl methanoate has no O–H group, so only dipole-dipole forces (and van der Waals) act between molecules, giving a low boiling temperature (32 °C). Ethanoic acid forms hydrogen bonds between its O–H groups; these are stronger, so more energy is needed to separate the molecules, giving a higher boiling temperature (118 °C).

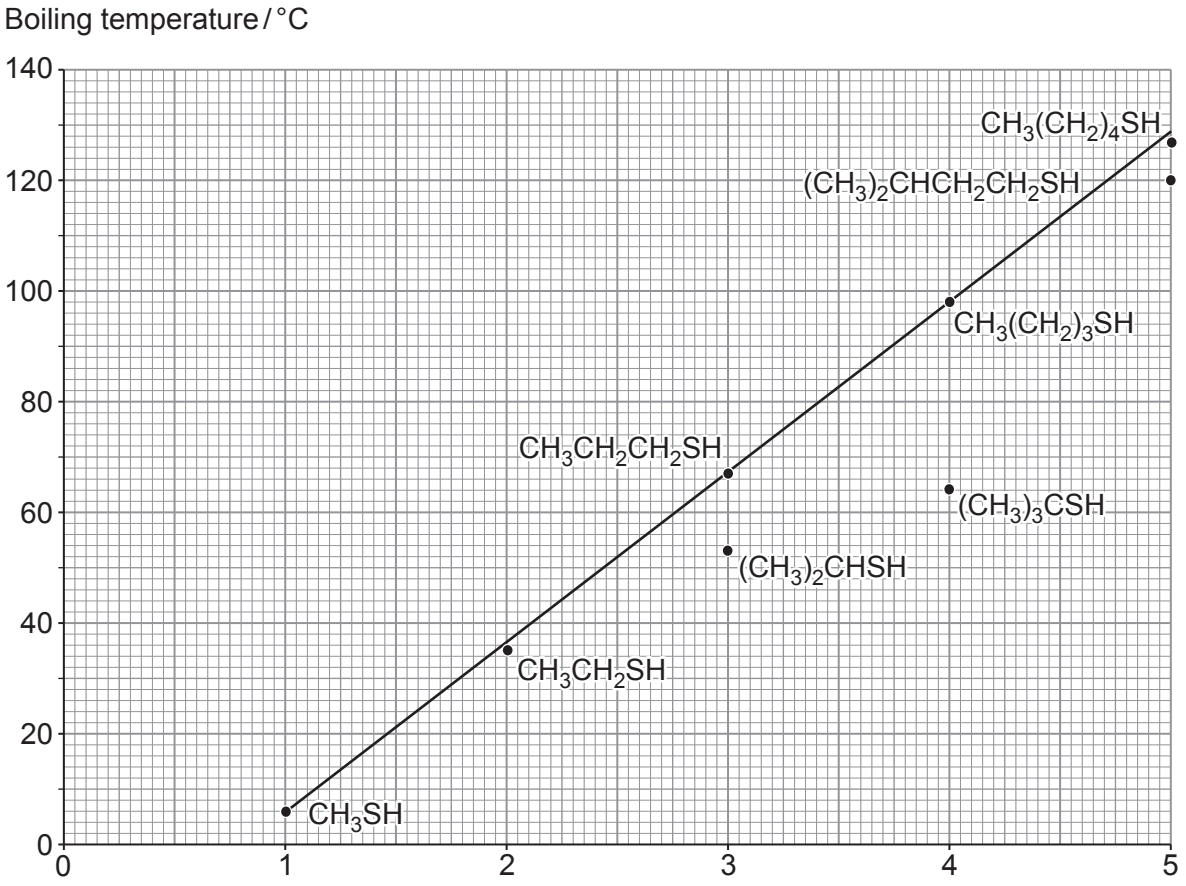
^{1}H NMR: methyl methanoate gives two peaks: the single HCOO hydrogen at about δ 9.8 ppm (8 to 10) and the CH_3O hydrogens at δ 3.3 to 4.3 ppm, peak area ratio 1 : 3 (3 : 1), with no splitting as there are no H atoms on adjacent carbons. Ethanoic acid also gives two singlets: the COOH hydrogen at about δ 11.0 ppm and the CH_3 hydrogens at δ 2.0 to 2.5 ppm (no splitting), area ratio 1 : 3.

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(b) The boiling temperatures of some thiols, R — SH, are shown in the graph.



(i) Predict the boiling temperature of hexanethiol. Give a reason for your answer. [2]

About 150 °C (in the range 140 to 160 °C).

Each extra CH_2 increases the boiling temperature by about 30 °C, as van der Waals forces increase with chain length.

(ii) Explain why branched chain thiols, with the same molecular formula, have a lower boiling temperature than their straight chain equivalents. [2]

Branched molecules have less surface area contact (pack less closely), so the intermolecular (van der Waals) forces are weaker.

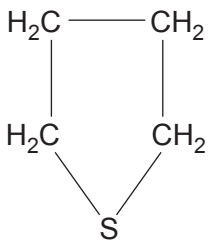
Less energy is needed to separate the molecules into the gas phase.

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(c) Tetrahydrothiophene (M_r 88) has been added to natural gas to give a warning signal of a gas leak.



This is because it has a very penetrating smell and only very small quantities are necessary. A typical concentration is 5 ppmv (parts per million by volume).

Show that to obtain this concentration, ~1.8 cm^3 of liquid tetrahydrothiophene is needed in 100 m^3 of natural gas at 298 K and 1 atm pressure.

You should assume that the density of tetrahydrothiophene is 1.0 g cm^{-3}. [3]

$100\ m^3 = 100 \times 10^3\ dm^3 = 1.0 \times 10^5\ dm^3$

5 ppmv: in $10^6\ dm^3$ there are 5 dm^3 of tetrahydrothiophene

so in $10^5\ dm^3$ there are 0.50 dm^3

moles = 0.50 ÷ 24.5 = 0.0204 mol (298 K, 1 atm)

mass = 0.0204 × 88 = 1.8 g

volume of liquid = mass ÷ density = 1.8 ÷ 1.0 = 1.8 cm^3

(d) The combustion of tetrahydrothiophene produces carbon dioxide, sulfur dioxide and water.

Write the equation for this reaction. [1]

$C_4H_8S + 7O_2 \rightarrow 4CO_2 + 4H_2O + SO_2$

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(e) Phenol (M_r 94) reacts with bromine to give 2,4,6-tribromophenol (M_r 331).

This reaction can be used to find the concentration of an aqueous solution of phenol.

An excess of aqueous bromine was added to 150 cm^3 of an aqueous solution of phenol. This reaction produced 4.58 g of 2,4,6-tribromophenol.

Calculate the mass of phenol dissolved in 150 cm^3 of this solution and hence its concentration in g dm^{-3}. [2]

moles of 2,4,6-tribromophenol = 4.58 ÷ 331 = 0.0138 mol

1 mol phenol gives 1 mol, so moles of phenol = 0.0138 mol

mass of phenol = 0.0138 × 94 = 1.30 g (in 150 cm^3)

concentration = 1.30 × 1000 ÷ 150 = 8.67 g dm^{-3}

Concentration = ... *8.67* ..... g dm^{-3}

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12. (a) (i) Lactose, found in milk, is classed as a reducing sugar because it reacts with Fehling's solution.

Describe what is seen when lactose reacts with Fehling's solution. [2]

The (deep) blue Fehling's solution

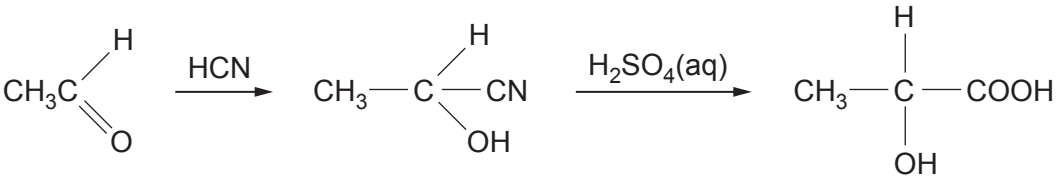
gives a red (brick-red / brown) precipitate on warming.

(ii) Give another compound that will reduce Fehling's solution in this way. [1]

propanal, CH_3CH_2CHO

(b) In industry, 2-hydroxypropanoic acid (lactic acid) is still largely made by the fermentation of dairy products.

A laboratory method of producing 2-hydroxypropanoic acid is from ethanal.



(i) State the name of the mechanism in the reaction between ethanal and hydrogen cyanide. [1]

nucleophilic addition

(ii) The second stage of this reaction involves hydrolysis of the intermediate compound 2-hydroxypropanenitrile.

State what is meant by the term hydrolysis. [1]

Decomposition (breaking down) of a compound by water (or dilute acid).

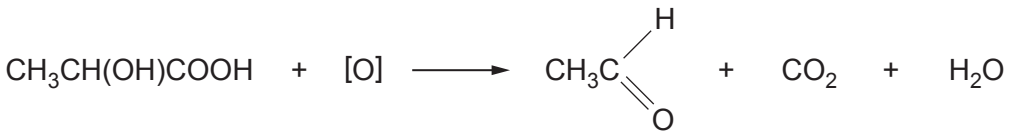
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(c) 2-Hydroxypropanoic acid can be converted back to ethanal by using a suitable oxidising agent.



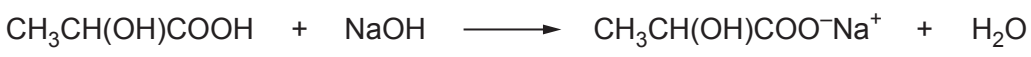
2-Hydroxypropanoic acid was oxidised and produced a 45% yield of ethanal. The boiling temperature of ethanal is 293 K.

Suggest **two** reasons for this low yield. [2]

1. *Ethanal is volatile (boils at 293 K, about room temperature), so some is lost by evaporation.*

2. *Further oxidation of ethanal to ethanoic acid (or incomplete oxidation / side reactions).*

(d) A 75 cm^3 sample of yoghurt was titrated against 0.200 mol dm^{-3} aqueous sodium hydroxide. 40.0 cm^3 was needed to just neutralise the lactic acid present in the yoghurt.



Calculate the percentage by volume of lactic acid (density 1.2 g cm^{-3}) in the yoghurt.

You should assume that lactic acid is the only acid present in the yoghurt. [3]

moles of NaOH = 0.200 × 40.0 ÷ 1000 = 0.00800 mol

moles of lactic acid = 0.00800 mol (1 : 1)

mass of lactic acid = 0.00800 × 90.06 = 0.720 g

volume of lactic acid = 0.720 ÷ 1.2 = 0.600 cm^3

percentage = 0.600 ÷ 75 × 100 = 0.80%

Percentage = *0.80* %

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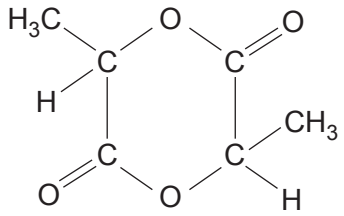
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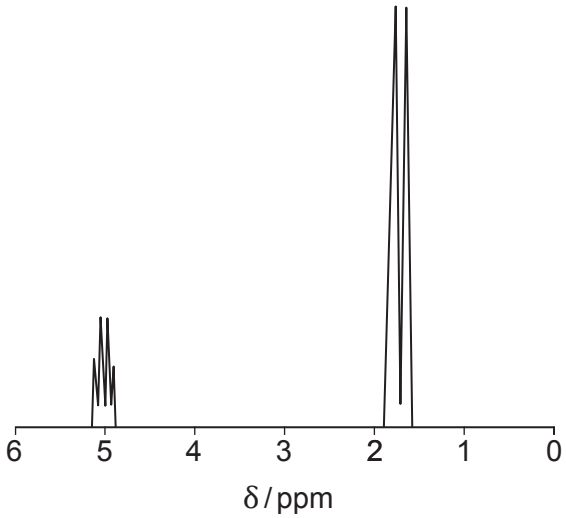
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(e) Lactic acid forms a 'lactide' by elimination of water between two molecules of the acid.



(i) A simplified high resolution ^{1}H NMR spectrum of this 'lactide' is shown below.



Use the structure of the 'lactide' to explain the splitting pattern seen in the NMR spectrum. [2]

The CH_3 (at 1.66 ppm) is a doublet since the adjacent carbon atom has one hydrogen atom bonded to it ($n + 1 = 2$).

The H (at 5.09 ppm) is a quartet since the adjacent carbon atom has three hydrogen atoms (CH_3) bonded to it.

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(ii) The infrared absorption spectrum of the 'lactide' shows strong absorptions at 1266 cm^{-1} and at 1750 cm^{-1}.

Use the **Data Booklet** and the structure of the 'lactide' to identify the bonds responsible for these absorptions in the 'lactide'. [1]

1266 cm^{-1}: C–O bond (1000 to 1300 cm^{-1})

1750 cm^{-1}: C=O bond (1650 to 1750 cm^{-1})

(iii) The 'lactide' is an intermediate in the formation of poly(lactic acid). The polymerisation occurs using a tin(II) octanoate catalyst.

Give the formula of tin(II) octanoate. [1]

$(CH_3(CH_2)_6COO)_2Sn$

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13. (a) Write a method for the preparation of pure 2-nitro-1-methylbenzene (boiling temperature 222°C), starting with methylbenzene (boiling temperature 111°C).

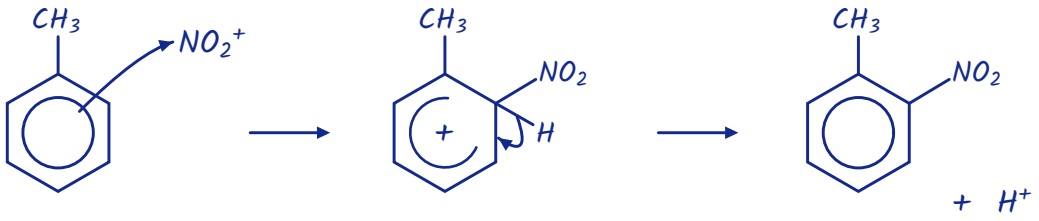
In your answer you should include

- the reagents used
- an equation
- a mechanism for the reaction and the name of the type of mechanism occurring

[6 QER]

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

Mechanism: electrophilic substitution (NO_2^+ is the electrophile)



$H^+ + HSO_4^- \rightarrow H_2SO_4$ *(catalyst regenerated)*

$C_6H_5CH_3 + HNO_3 \rightarrow CH_3C_6H_4NO_2 + H_2O$

Reagents: concentrated nitric acid and concentrated sulfuric acid (nitrating mixture). Add the nitrating mixture slowly, with stirring, to the methylbenzene in an ice bath, keeping the temperature below about 30 °C to avoid poly-nitration.

Pour the mixture onto ice/water and separate the organic layer with a separating funnel; wash it with sodium hydrogencarbonate solution then water, and dry it with anhydrous $MgSO_4$.

Other mono-nitrated isomers (mainly 4-nitro-1-methylbenzene) are also formed, so separate by fractional distillation, collecting the 2-nitro-1-methylbenzene fraction at about 222 °C (unreacted methylbenzene distils off first at 111 °C).

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(b) Further nitration of 2-nitro-1-methylbenzene gives polynitrated products. One of these is the solid 1-methyl-2,4-dinitrobenzene.

Outline how you would recrystallise a sample of this compound using ethanol as the solvent. [4]

Dissolve the sample in the minimum volume of hot ethanol.

Filter the hot solution (to remove insoluble impurities).

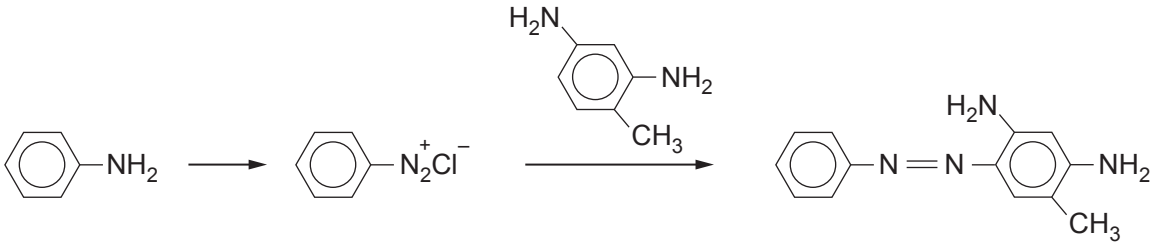
Allow the filtrate to cool so that crystals form (soluble impurities stay in solution).

Filter off the crystals (under reduced pressure), wash with a little cold ethanol and dry them.

(c) Give the reagents used to produce 1-methylbenzene-2,4-diamine from 1-methyl-2,4-dinitrobenzene. [1]

Sn (or Fe) and concentrated HCl

(d) The reaction sequence below shows the formation of the azo dye Basic Orange 1 from 1-methylbenzene-2,4-diamine and phenylamine.



(i) Give the reagent(s) needed to produce benzenediazonium chloride from phenylamine. [1]

$NaNO_2$ and HCl (HNO_2)

(ii) Give the temperature used in the reaction to produce benzenediazonium chloride. [1]

5 °C (below 10 °C)

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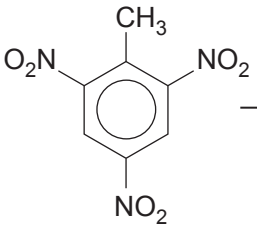
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(e) Further nitration of 1-methyl-2,4-dinitrobenzene gives 1-methyl-2,4,6-trinitrobenzene (TNT).

On detonation this explosive gives the products shown in the equation below.

Complete this equation by balancing it. [1]



$\longrightarrow$ 3CO + *3* C + CO_2 + 1.5 H_2 + 1.5 N_2 + H_2O

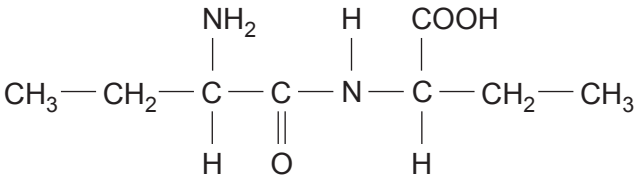
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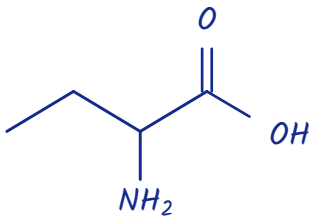
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14. (a) (i) I. Name the α-amino acid that forms the dipeptide whose formula is shown below. [1]

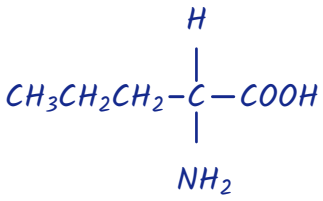


2-aminobutanoic acid

II. Give the **skeletal** formula of this α-amino acid. [1]



(ii) Draw the structure of an α-amino acid that has a relative molecular mass of 117. [1]



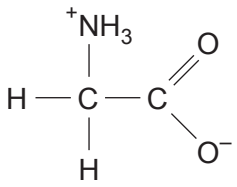
(2-aminopentanoic acid, M_r = 117)

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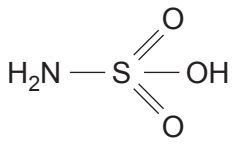
(b) (i) Aminoethanoic acid can exist as a zwitterion.



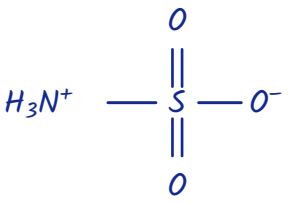
Explain why this results in a much higher melting temperature than expected. [1]

The zwitterions are held together by strong ionic forces (attraction between NH_3^+ and COO^- of neighbouring 'molecules'), so much more energy is needed to overcome them than weak intermolecular forces.

(ii) Sulfamic acid also exists as a zwitterion and has a similarly high melting temperature to aminoethanoic acid.



Suggest a structure for the zwitterion form of sulfamic acid. [1]



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(c) One way of making an ester is by reacting an acid chloride, R — COCl, with an alcohol.

(i) Give a reagent used to produce benzoyl chloride from benzoic acid. [1]

PCl_5 (phosphorus(V) chloride)

(ii) State why it is important to exclude moisture from the apparatus when preparing benzoyl chloride in this way. [1]

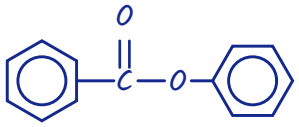
Benzoyl chloride (and PCl_5) react with (are hydrolysed by) water.

(iii) Benzoyl chloride reacts with phenol to give phenyl benzoate. This reaction is carried out in the presence of sodium hydroxide and therefore also gives sodium chloride and water.

I. Give the equation for this reaction. [2]

$C_6H_5OH + C_6H_5COCl + NaOH$

$\rightarrow C_6H_5COOC_6H_5 + NaCl + H_2O$



(phenyl benzoate)

II. Phenyl benzoate is produced as a solid, which is filtered off and recrystallised from ethanol.

The melting temperature of phenyl benzoate is 69°C.

If the phenyl benzoate still contained traces of the solvent, state how the melting temperature would be affected. [1]

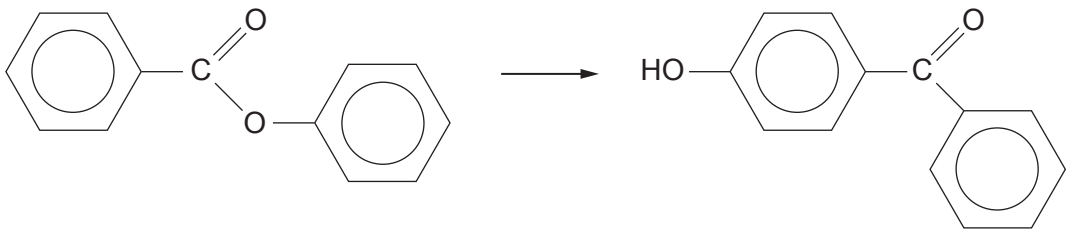
It would melt below 69 °C and over a range of temperatures.

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(d) Under suitable conditions phenyl benzoate can rearrange to give 4-hydroxybenzophenone.



(i) The mass spectrum of both compounds was taken.

Phenyl benzoate showed a strong signal at m/z 105 and 4-hydroxybenzophenone gave a strong signal at m/z 121.

Suggest a formula for each of these fragments. [1]

105 $C_6H_5CO^+$

121 $HOC_6H_4CO^+$ $(C_6H_4CO(OH)^+)$

(ii) The infrared absorption spectrum of 4-hydroxybenzophenone gave a strong absorption that was not present in the absorption spectrum of phenyl benzoate.

Use the formulae of the two compounds and the **Data Booklet** to suggest the bond responsible for this strong absorption and its appropriate wavenumber. [1]

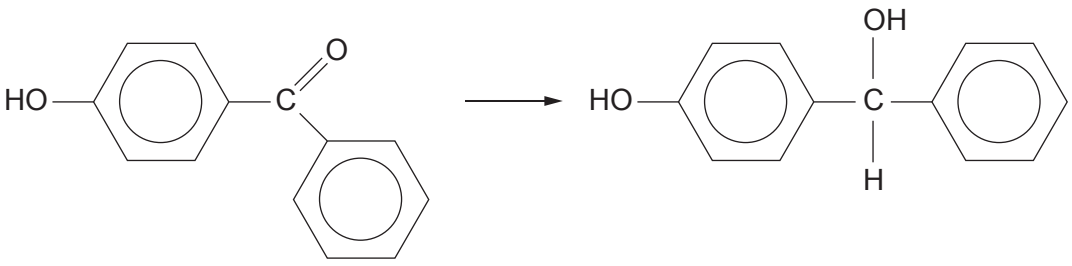
O–H (phenol) bond, broad absorption at 3200 to 3550 cm^{-1}

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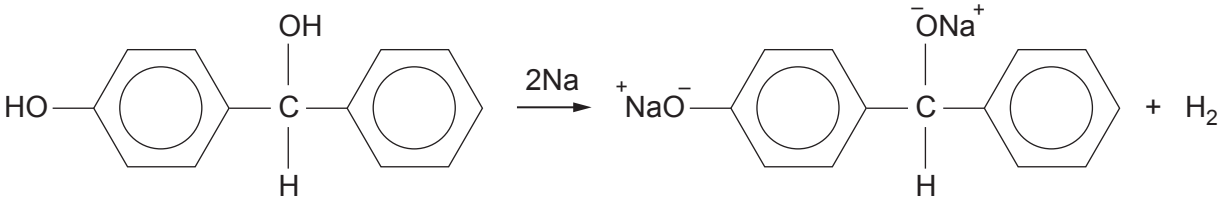
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(iii) Give a reducing agent for the reaction below. [1]



$NaBH_4$ (sodium tetrahydridoborate(III))

(iv) Alcohols and phenols react with sodium to produce hydrogen gas.



compound **A**

Calculate the volume of hydrogen produced at 373 K and 1 atm pressure if 0.020 mol of compound **A** reacts with sodium. [2]

0.020 mol A produces 0.020 mol H_2

volume at 298 K = 0.020 × 24.5 = 0.490 dm^3

$V_1/T_1 = V_2/T_2$ so $V_2 = 0.490 \times 373 \div 298$

$= 0.613\ dm^3$

Volume = *0.613* dm^3

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15. (a) (i) Microanalysis is an accurate procedure used to find the percentage of carbon and hydrogen in a compound. The compound is completely burned in oxygen at a high temperature, when these elements are turned into carbon dioxide and water.

From the results the masses of carbon and hydrogen present are found and the mass of oxygen present found by difference.

The following results were obtained for the analysis of a primary alcohol that only contains one oxygen atom in each molecule.

Mass of sample = 0.1940g

Mass of carbon dioxide produced = 0.4414 g

Mass of water produced = 0.1809 g

The percentage by mass of carbon in carbon dioxide is 27.27% and the percentage by mass of hydrogen in water is 11.21%.

Use the information given to find the masses of carbon and hydrogen in the sample and hence the mass of oxygen by difference.

From the data obtained find the empirical formula of the primary alcohol and its molecular formula. [5]

mass of C = 0.4414 × 27.27 ÷ 100 = 0.1204 g

mass of H = 0.1809 × 11.21 ÷ 100 = 0.0203 g

mass of O = 0.1940 − (0.1204 + 0.0203) = 0.0533 g

C : H : O = 0.1204/12.0 : 0.0203/1.01 : 0.0533/16.0

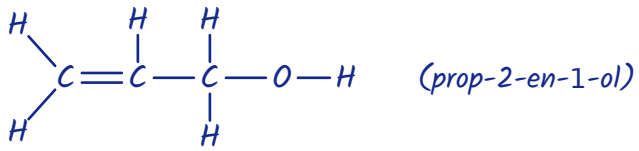
= 0.0100 : 0.0201 : 0.00333 = 3 : 6 : 1

only one O per molecule, so molecular = empirical formula (M_r = 58)

Empirical formula C_3H_6O

Molecular formula C_3H_6O

(ii) Give the **displayed** formula of the primary alcohol. [1]



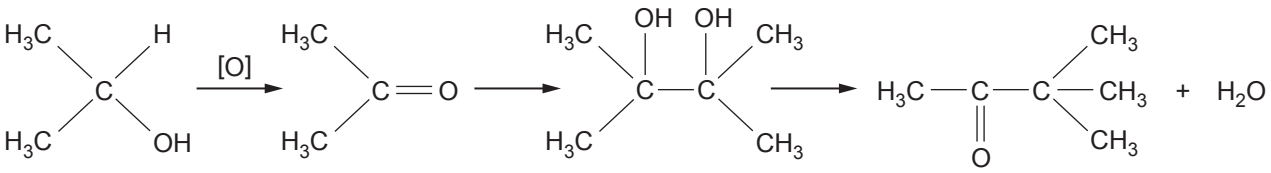
(prop-2-en-1-ol)

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(b) Study the reaction sequence and answer the questions that follow.



propan-2-ol propanone pinacol pinacolone

(i) Give an oxidising agent used to produce propanone. [1]

acidified potassium dichromate ($K_2Cr_2O_7$ / H_2SO_4)

(ii) State why the production of pinacol from propanone is described as reduction. [1]

Hydrogen is being added (the C=O groups gain hydrogen to form C–OH groups).

(iii) Describe the ^{13}C NMR spectrum of pinacol, giving the number of signals and their approximate position. Use the **Data Booklet**. [2]

Two signals: the two central C–O carbons at δ 50 to 90 ppm and the four methyl carbons at δ 5 to 40 ppm.

(iv) I. State why both propan-2-ol and pinacolone undergo the triiodomethane reaction. [1]

Both contain the CH_3CO group (pinacolone) or its precursor, the $CH_3CH(OH)$ group (propan-2-ol).

II. Give the reagents used in the triiodomethane test and the observation for a positive test. [2]

Iodine and sodium hydroxide (I_2 / NaOH), warm.

Positive test: pale yellow precipitate (solid) of CHI_3.

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(v) The conversion of pinacol to pinacolone is described both as a rearrangement and an elimination.

Explain what you understand by these two terms. [2]

Rearrangement *a movement of atoms within the structure (a methyl group moves to the adjacent carbon).*

Elimination *removal (loss) of a small molecule, here water, from the molecule.*

15

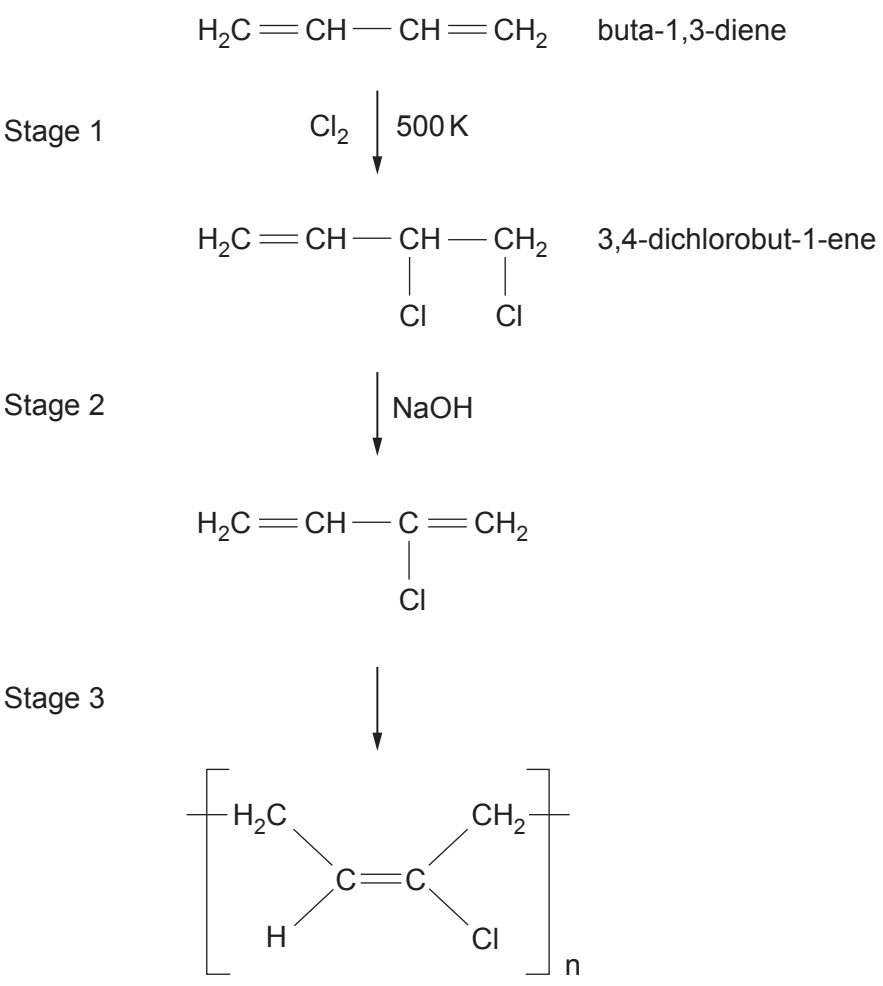
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16. (a) The polymer Neoprene has been used in face masks during the Covid-19 pandemic.

This synthetic rubber can be made by the following sequence of reactions.

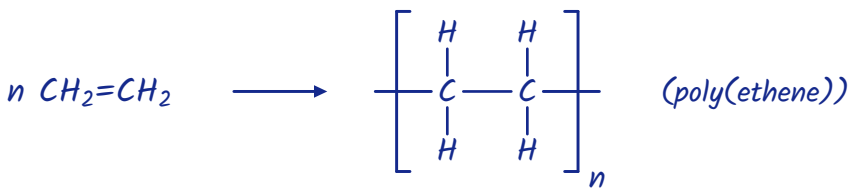


(i) State the type of reaction occurring during stage 2. [1]

elimination (dehydrohalogenation)

(ii) Stage 3 is described as addition polymerisation.

Give an equation showing another addition polymerisation of your choice. [1]



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(iii) State a difference between addition polymerisation and condensation polymerisation. [1]

A small molecule (e.g. water) is eliminated during condensation polymerisation, but not in addition polymerisation.

(b) The addition of bromine to but-2-ene gives 2,3-dibromobutane.

This halogenoalkane has several optical isomers.

State the effect that these isomers have on the plane of plane polarised light. [1]

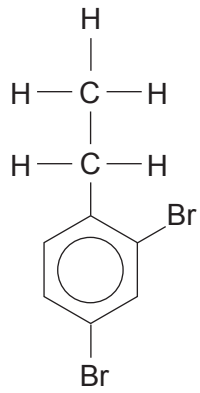
They rotate the plane of plane polarised light (to the left or to the right).

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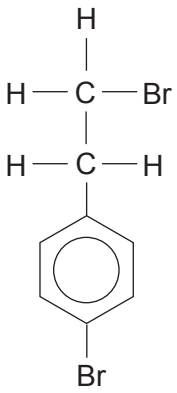
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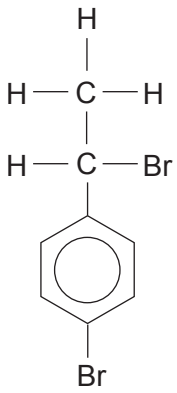
(c) Five isomers of formula $C_8H_8Br_2$ are shown below.



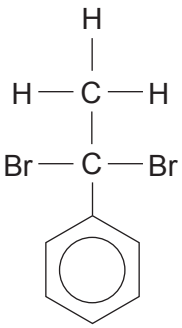
compound **R**



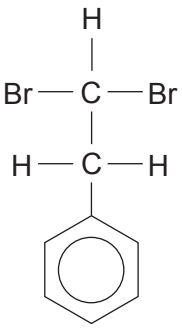
compound **S**



compound **T**



compound **U**



compound **V**

(i) State why compound **R** does not react with aqueous sodium hydroxide. [1]

Both Br atoms in R are bonded to the aromatic ring, and such Br atoms are not susceptible to attack by nucleophiles (OH^-).

(ii) Compounds **S**, **T**, **U** and **V** are dissolved in a suitable solvent and then warmed with aqueous sodium hydroxide.

State what is seen when excess aqueous nitric acid is added followed by aqueous silver nitrate. [1]

cream (off-white) precipitate

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(iii) 5.50 cm^3 of an impure sample of compound **S** (M_r 264) reacted with silver nitrate to give 5.69 g of silver bromide, AgBr (M_r 188).

The density of compound **S** is 1.73 g cm^{-3}.

Calculate the percentage purity of this sample of compound **S**. [4]

mass of S = 5.50 × 1.73 = 9.52 g

moles of S (if pure) = 9.52 ÷ 264 = 0.0360 mol

S : AgBr = 1 : 1, so 0.0360 mol AgBr

mass of AgBr (if pure) = 0.0360 × 188 = 6.77 g

percentage purity = 5.69 ÷ 6.77 × 100 = 84.0%

Percentage purity = 84.0 %

(iv) Describe how low resolution ^{1}H NMR can distinguish between the aliphatic side-chains of compounds **S** and **T**. Refer to both compounds in your answer. [2]

Compound S ($-CH_2CH_2Br$) gives two signals in a 1 : 1 peak area ratio.

Compound T ($-CHBrCH_3$) gives two signals in a 3 : 1 peak area ratio.

(v) State why high resolution ^{1}H NMR will give an unsplit signal for the aliphatic side-chains of compound **U**. [1]

In U ($-CBr_2CH_3$) the CH_3 hydrogens are bonded to a carbon atom whose adjacent carbon has no hydrogen atoms, so there is no splitting.

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GCE A LEVEL

A410U20-1A

S23-A410U20-1A

MONDAY, 19 JUNE 2023 – AFTERNOON

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

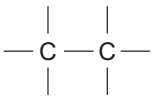
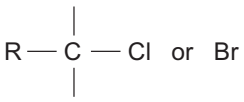
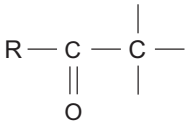
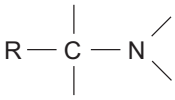
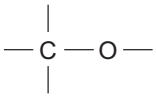
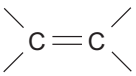
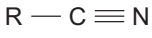
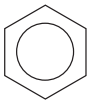
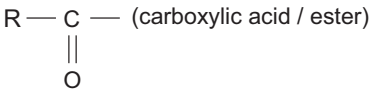
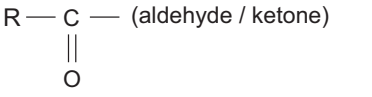
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Infrared absorption values

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

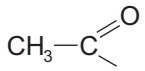
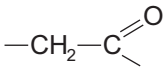
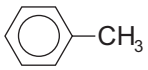
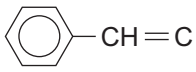
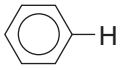
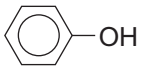
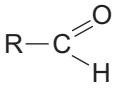
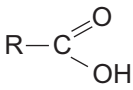
^{13}C NMR chemical shifts relative to TMS = 0

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

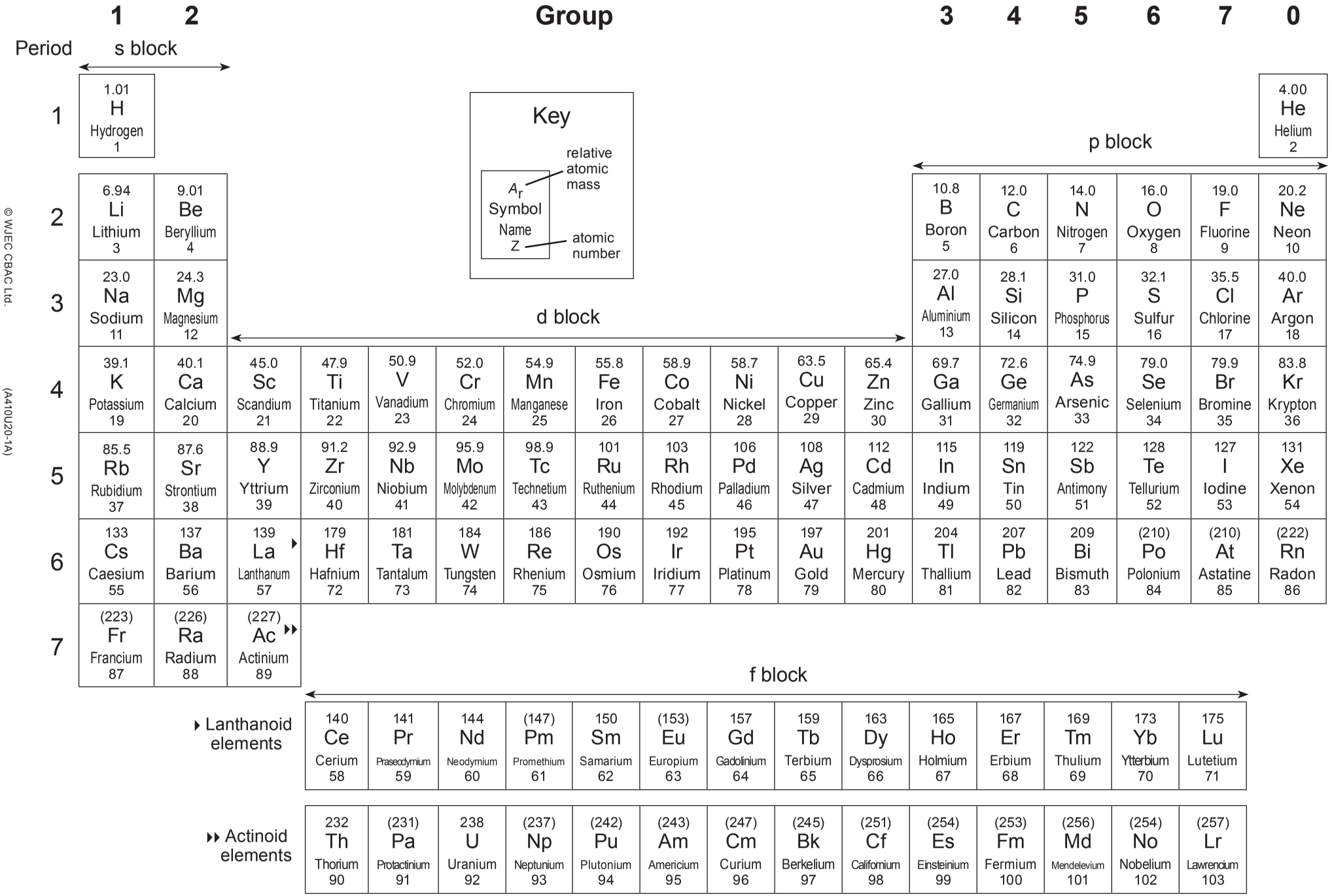
Type of proton	Chemical shift, δ (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
	2.0 to 2.5
	2.0 to 3.0
	2.2 to 2.3
HC—Cl or HC—Br	3.1 to 4.3
HC—O	3.3 to 4.3
R—OH	4.5 *
—C=CH	4.5 to 6.3
—C=CH—CO	5.8 to 6.5
	6.5 to 7.5
	6.5 to 8.0
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

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THE PERIODIC TABLE



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