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

GCE A LEVEL

A410U20-1

S24-A410U20-1

TUESDAY, 18 JUNE 2024 – MORNING

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 6.**	**15**	
Section B	**7.**	**17**	
	8.	**20**	
	9.	**18**	
	10.	**16**	
	11.	**18**	
	12.	**16**	
	Total	**120**	

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ADDITIONAL MATERIALS

- A calculator, pencil and ruler
- **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 **Q10**(a) and **Q12**(a).

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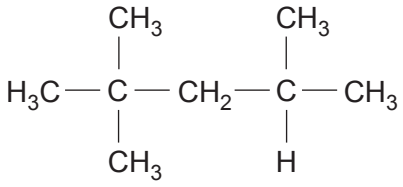
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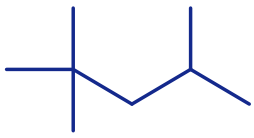
SECTION A

Answer **all** questions.

1. The structure of 2,2,4-trimethylpentane is shown below.



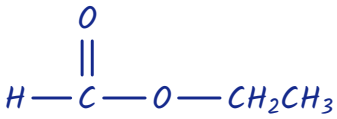
(a) Give the **skeletal** formula of this compound. [1]



(b) Give the equation for the complete combustion of 2,2,4-trimethylpentane. [1]

$(CH_3)_3CCH_2CH(CH_3)_2 + 12½O_2 \rightarrow 8CO_2 + 9H_2O$

2. Give the structure of an isomer of formula $C_3H_6O_2$ that produces a red precipitate with Fehling's reagent. Give your reasoning. [2]



ethyl methanoate

It contains an aldehyde (H–C=O, CHO) group, so it reduces Fehling's reagent (Cu^{2+}) to a red precipitate of Cu_2O.

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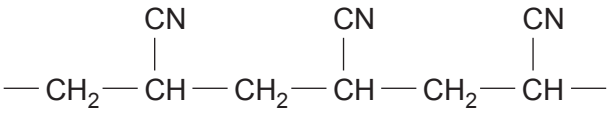
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3. State the name of an alcohol that produces phenylethene when it is dehydrated by heating with sulfuric acid. [1]

1-phenylethanol

4. The formula of a section of an addition polymer is shown below.



State the **name** of the monomer that can produce this polymer. [1]

prop-2-enenitrile

5. The oxidation of an alcohol containing only carbon, hydrogen and oxygen gave a monobasic carboxylic acid, R — COOH.

On heating 4.26 g of the silver salt of this acid, R — COOAg, 2.54 g of silver was produced.

(a) Find the relative molecular mass of the acid. [2]

$n(Ag) = 2.54 \div 108 = 0.0235$ mol $= n(RCOOAg)$

M_r of silver salt $= 4.26 \div 0.0235 = 181$

M_r of acid $= 181 - 108 + 1 = 74$

M_r = 74

(b) Use your answer to (a) to find the relative molecular mass of the R group and hence the formula of the alcohol. [2]

M_r of R $= 74 - 45$ (COOH) $= 29$, so R is C_2H_5

acid is CH_3CH_2COOH (propanoic acid)

alcohol: $CH_3CH_2CH_2OH$ (propan-1-ol)

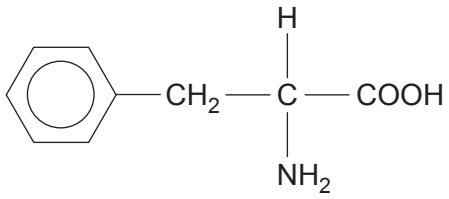
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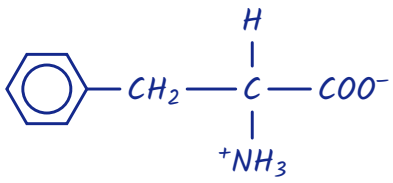
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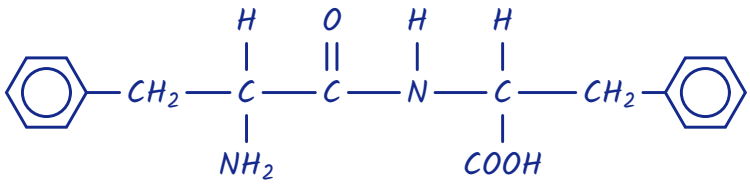
6. The formula for phenylalanine is shown below.



(a) Give the formula for the zwitterion of phenylalanine. [1]



(b) Give the structure of the dipeptide produced from two molecules of phenylalanine. [1]



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(c) The solubility of phenylalanine at two temperatures is shown in the table.

Temperature / °C	Solubility / g per 100 g of water
25	1.41
100	6.89

A saturated solution containing 50 g of water is cooled from 100 °C to 25 °C. Calculate the mass of phenylalanine precipitated. [1]

6.89 − 1.41 = 5.48 g per 100 g of water

for 50 g of water: 5.48 × 50 ÷ 100 = 2.74 g

Mass = 2.74 g

(d) Amino acids produce nitrogen gas when reacted with nitric(III) acid.

3.40 g of a damp sample of phenylalanine (M_r 165) was dissolved in water and reacted with nitric(III) acid.

$$C_6H_5CH_2CH(NH_2)COOH + HNO_2 \longrightarrow N_2 + C_6H_5CH_2CH(OH)COOH + H_2O$$

The sample produced 490 cm^3 of nitrogen gas, measured at 298 K and 1 atm. Show that the purity of the phenylalanine is 97.1%. [2]

$n(N_2) = 490 \div 24\,500 = 0.0200$ mol

mole ratio 1 : 1, so n(phenylalanine) = 0.0200 mol

mass of phenylalanine = 0.0200 × 165 = 3.30 g

purity = 3.30 ÷ 3.40 × 100 = 97.1 %

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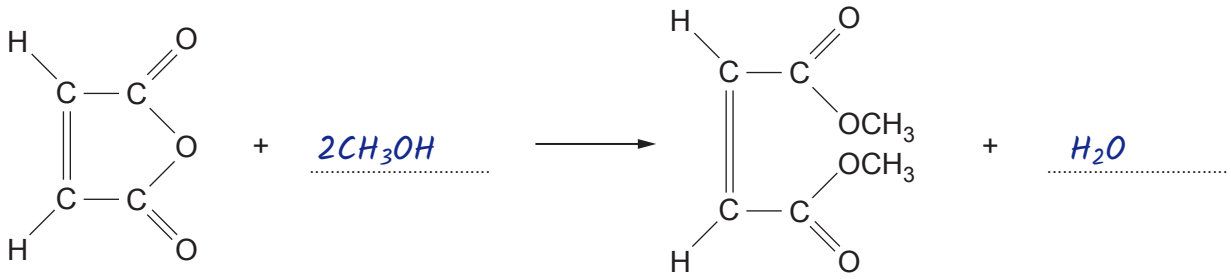
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SECTION B

Answer **all** questions.

7. In industry, dimethyl maleate is produced from maleic anhydride and methanol.

(a) Complete the equation for this reaction. [2]



dimethyl maleate

(b) The low resolution ^{1}H NMR spectrum of dimethyl maleate shows one signal for the H — C ═ protons and one for the — OCH_3 protons.

Use the **Data Booklet** to complete the table below. [2]

Proton	Chemical shift, δ / ppm	Relative peak area
H — C ═	6.2	1
— OCH_3	3.8	3

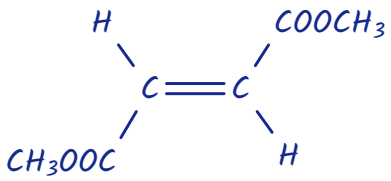
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(c) Dimethyl fumarate and dimethyl maleate are the *E-Z* stereoisomers of dimethyl ethenedioate.

Draw the structure of dimethyl fumarate. [1]



(d) Dimethyl maleate can be isomerised to dimethyl fumarate by using bromine in the presence of ultraviolet light.

(i) In an experiment 0.5 cm^3 of a 1.0 mol dm^{-3} bromine solution was used. The bromine acts as a catalyst in this reaction.

Calculate the number of moles of bromine in this solution. [1]

$n = (0.5 \div 1000) \times 1.0 = 5.0 \times 10^{-4}$ mol

Number of moles = 5.0×10^{-4} mol

(ii) Ultraviolet light causes initial homolytic fission of the bromine molecule into two bromine radicals.

State the number of outer electrons present in a bromine radical. [1]

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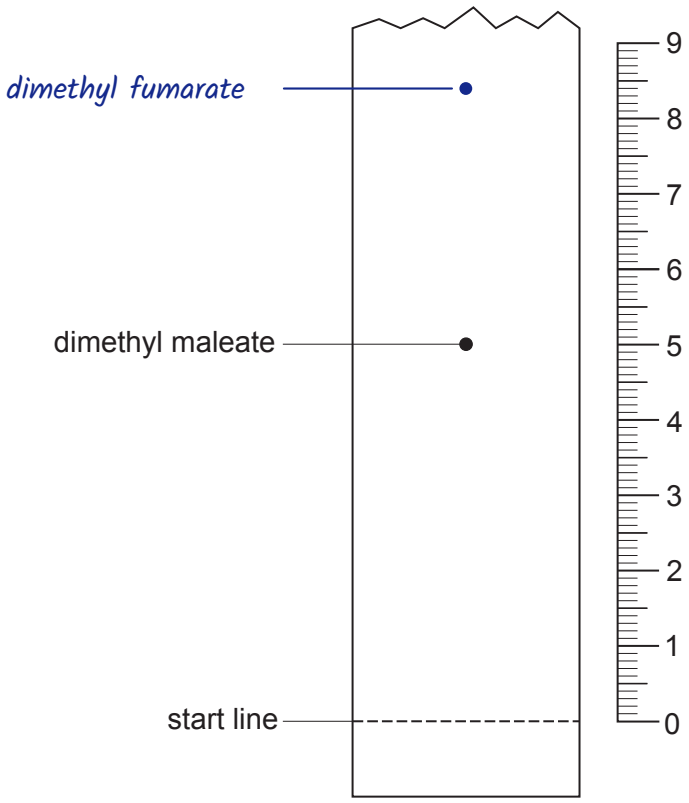
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(iii) The progress of the reaction can be followed by using thin-layer chromatography.

As the reaction proceeds the spot due to the dimethyl fumarate becomes more intense whereas the spot due to the dimethyl maleate fades.

The diagram below shows the spot due to dimethyl maleate, which has an R_f value of 0.34.

Draw a spot on the chromatogram to show the presence of dimethyl fumarate, which has an R_f value of 0.57. [1]



(iv) At the end of the reaction, solid dimethyl fumarate is filtered off.

The melting temperature of pure dimethyl fumarate is 104 °C.

A student carried out this reaction and found that the melting temperature of his dimethyl fumarate sample was in the range 89-96 °C, showing that it was impure.

Suggest **two** impurities that might be present in the sample. [2]

1. (unreacted) dimethyl maleate

2. bromine (solution) or water

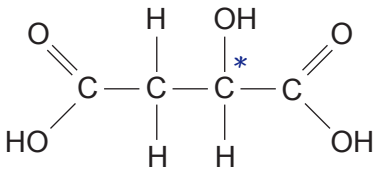
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(e) 2-Hydroxybutanedioic acid (malic acid) has important uses in the food industry.

(i) Use an asterisk (*) to indicate the position of a chiral centre in the structure of malic acid. [1]



(ii) Malic acid is one of the acidic compounds found in apples. Only one of the two enantiomers is present.

When malic acid is produced synthetically equal quantities of both enantiomers are produced.

Explain why an aqueous solution of synthetic malic acid has no effect on the plane of plane-polarised light. [1]

Each enantiomer rotates the plane of plane-polarised light by the same amount in opposite directions, so the racemic mixture gives zero rotation.

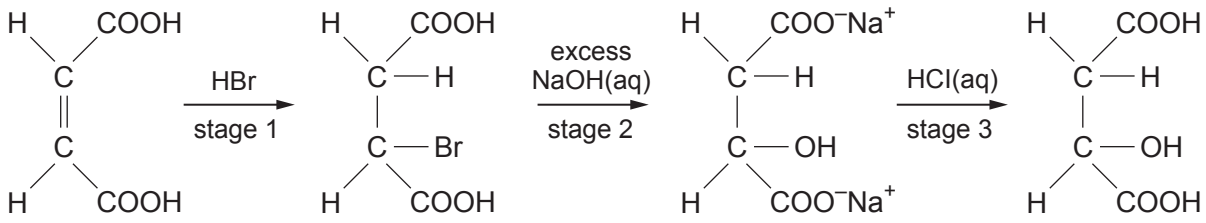
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(iii) One method to prepare malic acid from maleic acid is shown in the reaction sequence below.



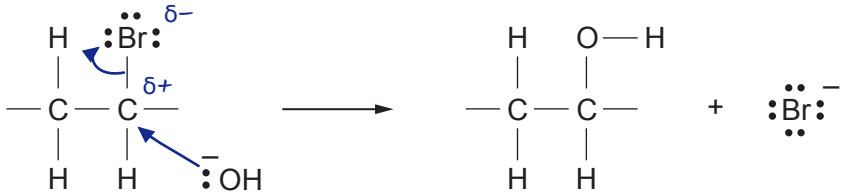
maleic acid malic acid

I. Stage 1 is described as an electrophilic addition reaction.

Give the formula of the electrophile used in this stage. [1]

H^+ ($H^{\delta+}$ of HBr)

II. A bromine atom is substituted by an —OH group in stage 2. Complete the mechanism for the reaction by using curly arrows and appropriate partial charges. [2]



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III. Explain why it is necessary to use an **excess** of aqueous sodium hydroxide in stage 2. [1]

If not in excess, the added sodium hydroxide will simply neutralise the two COOH groups present, leaving no OH^- to substitute Br.

IV. Discuss why the C — Br bond is broken via heterolytic fission in stage 2. [1]

Bromine has a higher electronegativity than carbon ($C^{\delta+}$–$Br^{\delta-}$), so the bromine atom attracts both electrons from the C–Br bond and leaves as Br^-.

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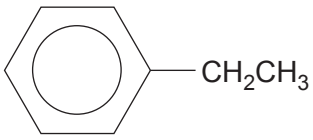
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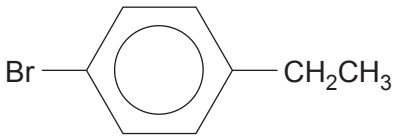
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8. (a) A student was asked for a method to produce 4-bromo-1-ethylbenzene, starting from ethylbenzene.



ethylbenzene



4-bromo-1-ethylbenzene

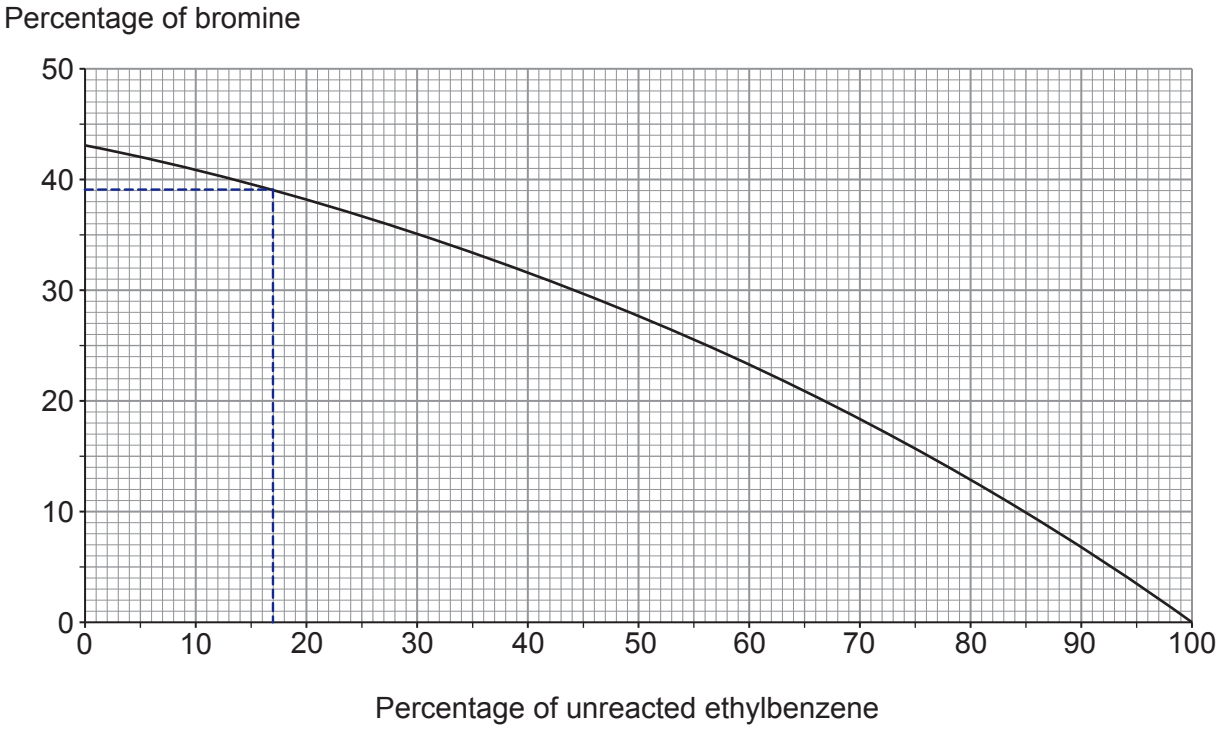
(i) State the reagent(s) needed for this reaction. [1]

bromine and iron(III) bromide, Br_2 and $FeBr_3$

(ii) The organic products of the reaction contained some unreacted ethylbenzene as well as bromine-containing reaction products.

The percentage of bromine in these products was 39.

Use the graph to find the percentage of unreacted ethylbenzene. [1]



Percentage = *17* %

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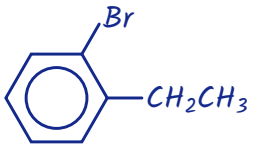
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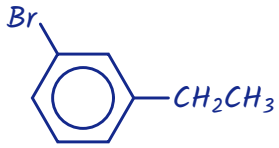
(iii) An HPLC chromatogram was taken of the organic products of the reaction.

Apart from unreacted ethylbenzene there were four other signals.

I. Three signals resulted from products with a relative molecular mass of 185. One of these is 4-bromo-1-ethylbenzene.

Suggest structures for the other two compounds with this relative molecular mass. Give a reason for your answer. [2]



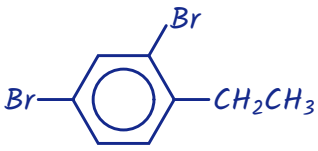


2-bromo-1-ethylbenzene 3-bromo-1-ethylbenzene

Substitution can also occur elsewhere in the ring (2- or 3-position).

II. The fourth compound had the molecular formula $C_8H_8Br_2$.

Suggest a structure for this compound. [1]



(b) Give reagent(s) that can be used to convert (1-bromoethyl)benzene, $C_6H_5CHBrCH_3$, into phenylethene, $C_6H_5CH=CH_2$. State why this is classed as an elimination reaction. [2]

Sodium hydroxide dissolved in ethanol (alcoholic NaOH), heated.

A small molecule, HBr, is removed (from adjacent carbons), forming a C=C.

(c) A sample of ethylbenzene is contaminated with phenylethene.

Give a test that would confirm the presence of phenylethene in this sample. State the reagent used and the expected observation. [2]

Add aqueous bromine dropwise: the bromine is decolourised (orange to colourless).

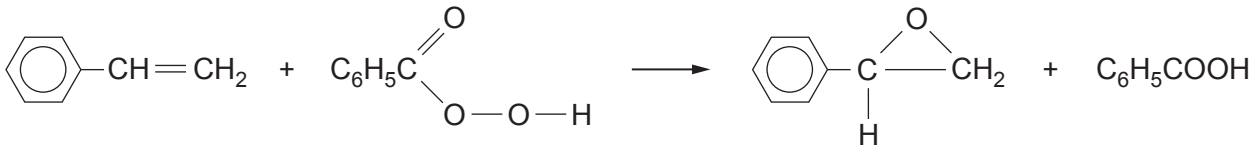
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(d) Phenylethene reacts with peroxybenzoic acid, C_6H_5COOOH, to give phenyloxirane.



M_r 104 M_r 120

phenyloxirane

In a preparation, 3.00 g of phenylethene is added slowly to a solution of a slight excess of peroxybenzoic acid dissolved in 500 cm^3 of trichloromethane. The mixture is kept at 0 °C and stirred for 24 hours.

The products are then placed in a separating funnel and shaken with an excess of aqueous sodium hydroxide. The layers are allowed to separate and the trichloromethane layer removed. This layer is washed with water to remove traces of sodium hydroxide and then dried. The trichloromethane is removed by distillation, leaving phenyloxirane, which is collected by distillation at 188-192 °C. The yield of phenyloxirane is 2.50 g.

(i) Suggest why aqueous sodium hydroxide is added to the products. [2]

To react with the benzoic acid produced (and excess peroxyacid) to give water-soluble sodium benzoate, which is removed in the aqueous layer.

(ii) Two layers are formed in the separating funnel. The trichloromethane layer is the lower layer.

State why trichloromethane forms the lower layer. [1]

Trichloromethane is denser than water (the aqueous layer).

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(iii) Calculate the percentage yield of phenyloxirane. [3]

n(phenylethene) = 3.00 ÷ 104 = 0.0288 mol

n(phenyloxirane) = 2.50 ÷ 120 = 0.0208 mol

mole ratio 1 : 1, so theoretical = 0.0288 mol

% yield = 0.0208 ÷ 0.0288 × 100 = 72.2 %

Percentage yield = *72.2* %

(e) A sample of phenylethane-1,2-diol is contaminated with a small quantity of phenylethanal.

Explain how the infrared absorption spectrum of this impure sample would indicate the presence of phenylethanal. [2]

A peak would be seen between 1650 and 1750 cm^{-1}, indicating the presence of the C=O group (absent from the diol).

(f) Complete the table below. Give the observations made, if any, when phenylethanal and phenylethanone are tested with the reagents shown. [3]

Test	phenylethanal $C_6H_5CH_2CHO$	phenylethanone $C_6H_5C(O)CH_3$
alkaline iodine	*no observable reaction*	*yellow precipitate formed*
Tollens' reagent	*silver mirror formed*	*no observable reaction*
warming with acidified potassium dichromate	*turns from orange to green*	*no observable reaction*

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9. (a) Octane has a boiling temperature of 125 °C. It can be made by reacting 1-bromobutane or 1-iodobutane with sodium.

The equation shows the reaction of 1-bromobutane. The equation using 1-iodobutane is similar.

$$2CH_3CH_2CH_2CH_2Br + 2Na \longrightarrow C_8H_{18} + 2NaBr$$

The table shows some relevant information.

Halogenoalkane	M_r	Boiling temperature / °C	Yield of octane / %
1-bromobutane	137	102	27
1-iodobutane	184	131	30

Use this information to suggest **two** disadvantages of using 1-iodobutane as a starting material to make octane. [2]

1. 1-Iodobutane (131 °C) and octane (125 °C) have similar boiling temperatures, so separation by distillation is difficult.

2. A greater mass of 1-iodobutane (M_r 184) is needed than 1-bromobutane for a similar yield, i.e. lower atom economy.

(b) The radical chlorination of butane produces 2-chlorobutane as one of the products.

One stage in this reaction is the formation of the 2-butyl radical.

Complete the equation below that shows its formation. [2]

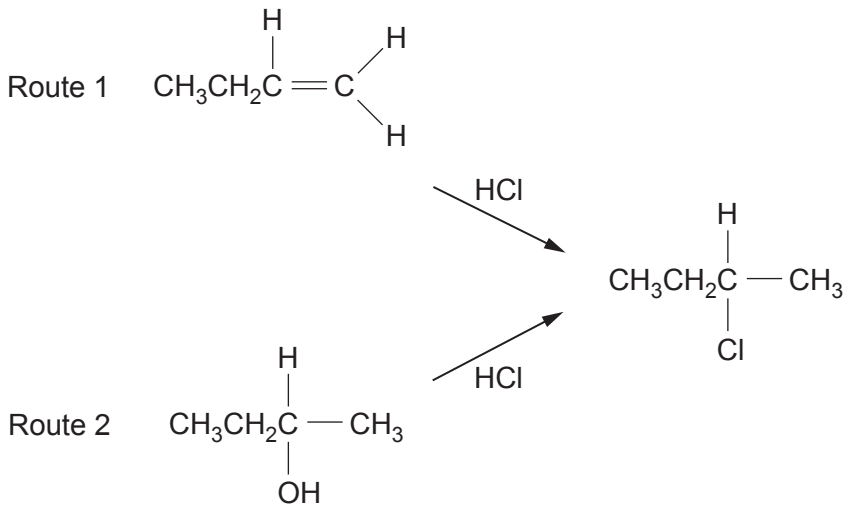
$CH_3CH_2CH_2CH_3 + Cl\bullet \longrightarrow$ $CH_3CH_2C\bullet HCH_3$ + HCl

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(c) The diagram shows two other routes to produce 2-chlorobutane.



(i) State the name of the mechanism occurring in route 1. [1]

electrophilic addition

(ii) State the name of a catalyst that can be used in route 2. [1]

zinc chloride, $ZnCl_2$

(iii) Suggest why route 2 may give a higher yield of 2-chlorobutane than route 1. [1]

Route 2 can give only one mono-chlorinated product, whereas in route 1 some 1-chlorobutane is also produced (HCl can add across the C=C either way).

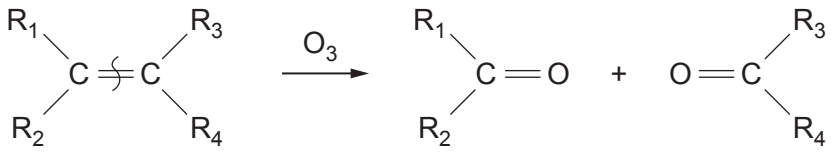
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(d) The reaction of an alkene with ozone (ozonolysis) can be used to find the position of the C = C double bond in compound **T**.



compound **T**

(i) Chemical analysis of compound **T** showed that it contains 85.7% of carbon and 14.3% of hydrogen by mass.

Explain why this is **not** helpful in finding the structure of compound **T**. [1]

All alkenes containing one C=C have the same percentages of carbon and hydrogen; it only gives the empirical formula, CH_2.

(ii) Explain why compound **T cannot** be cycloheptane, despite it containing the correct percentages of carbon and hydrogen by mass. [1]

Cycloheptane is not an alkene; it does not contain a C=C double bond.

(iii) Ozonolysis of compound **T** produced two **different** ketones.

Explain what can be deduced about the structure of compound **T** from this statement. [2]

T cannot be a symmetrical alkene; the double bond cannot be in the middle of the carbon chain, and at least one of R_1 to R_4 must be different to the others.

Each C=C carbon carries two alkyl groups (no H), so no aldehyde forms.

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(iv) Both of the ketones produced by the ozonolysis reaction gave a positive triiodomethane reaction.

Give the formula of the group that must be present in both of these ketones. [1]

$CH_3C{=}O$ (a CH_3CO- group)

(v) At 426 K and 1 atm, 4.90 g of compound **T** has a volume of 1.75 dm^3. The molar gas volume under these conditions is 35.0 dm^3.

Use this information to show that the relative molecular mass of compound **T** is 98. [1]

$n = 1.75 \div 35.0 = 0.0500$ mol

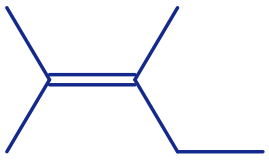
$M_r = 4.90 \div 0.0500 = 98$

(or $M_r = 4.90 \times 35.0 \div 1.75 = 98$)

(vi) Use your answers to parts (i)-(v) to suggest a structure for compound **T**. [2]

C_7H_{14} (M_r 98); ozonolysis gives propanone and butanone, two different ketones, both containing $CH_3C{=}O$.

$(CH_3)_2C{=}C(CH_3)CH_2CH_3$



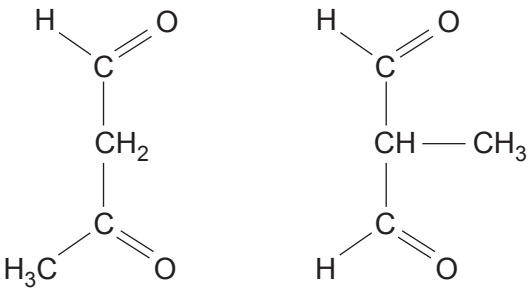
2,3-dimethylpent-2-ene

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(e) The formulae of compounds **Q** and **R** are shown below. Both are aldehydes.



compound **Q** compound **R**

Discuss the differences in the splitting patterns of the high resolution ^{1}H NMR spectra of these two compounds.

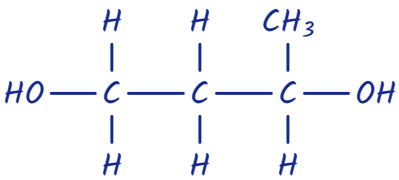
Splitting due to the aldehyde protons should be ignored.

The position of the signals is not required. [2]

Compound Q shows a singlet for both the CH_2 and the CH_3 protons, as there are no H atoms on the adjacent carbons.

Compound R shows a quartet for the CH proton (next to CH_3) and a doublet for the CH_3 protons (next to CH).

(f) Draw the structure of the compound produced when compound **Q** reacts with excess sodium tetrahydridoborate, $NaBH_4$. [1]



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10. (a) Esters can be converted into carboxylic acids by heating with aqueous sodium hydroxide, followed by acidification of the resulting salt of the carboxylic acid.

You are given 10 cm^3 of methyl benzoate and are asked to devise a method for the production of a sample of benzoic acid.

As part of your answer you should state the mass of methyl benzoate used and hence the volume of the sodium hydroxide solution required.

Your answer should also describe how to obtain a dry sample of benzoic acid from the reaction.

The following information is provided to help you in devising your method.

- The density of methyl benzoate is 1.09 g cm^{-3}
- Methyl benzoate is immiscible with water
- A slight excess of 1.00 mol dm^{-3} aqueous sodium hydroxide is required for complete hydrolysis of the ester [6 QER]

Mass of methyl benzoate = 10 × 1.09 = 10.9 g. M_r of $C_6H_5COOCH_3$ = 136, so moles = 10.9 ÷ 136 = 0.080 mol.

$C_6H_5COOCH_3$ + NaOH → C_6H_5COONa + CH_3OH (1 : 1), so 0.080 mol of NaOH = 80 cm^3 of 1.00 mol dm^{-3}; use a slight excess, about 90 cm^3.

Heat the mixture under reflux (with anti-bumping granules) until only one layer is present (the oily ester layer disappears).

Allow the mixture to cool, then acidify with hydrochloric acid; benzoic acid precipitates as a white solid: C_6H_5COONa + HCl → C_6H_5COOH + NaCl.

Cool in ice, filter (under reduced pressure) and wash the precipitated benzoic acid with a little cold water.

Dry the product between filter papers or in a desiccator (or low-temperature oven).

If a purer sample is needed, recrystallise the benzoic acid from the minimum volume of hot water before drying.

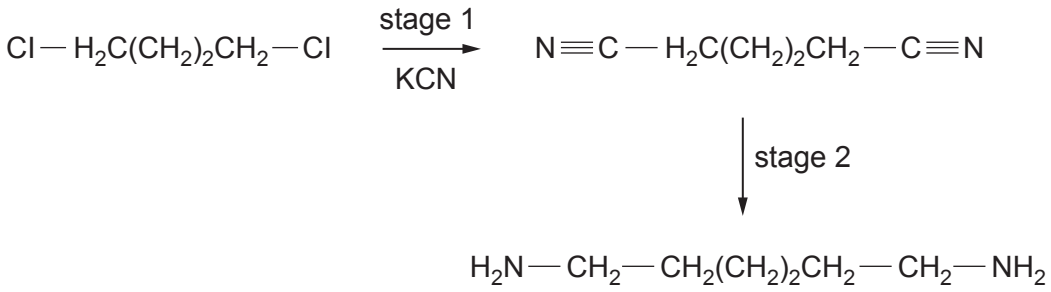
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(b) Nylon 6,10 can be made by reacting 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$, with decanedioyl dichloride, $ClOC(CH_2)_8COCl$.

(i) The flow chart shows a method for producing 1,6-diaminohexane from 1,4-dichlorobutane.



I. Give the equation for the reaction of potassium cyanide with 1,4-dichlorobutane in stage 1. [1]

$ClCH_2(CH_2)_2CH_2Cl + 2KCN \rightarrow NC(CH_2)_4CN + 2KCl$

II. The mechanism in stage 1 is described as nucleophilic substitution.

Give the formula of the nucleophile used in this stage. [1]

CN^-

III. State a reducing agent that can be used in stage 2. [1]

$LiAlH_4$ (lithium tetrahydridoaluminate(III))

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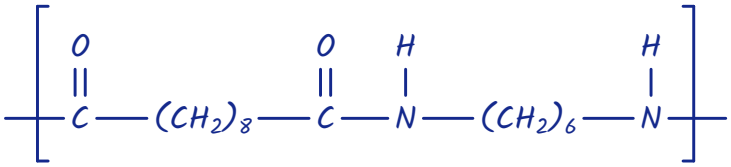
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(ii) Decanedioyl dichloride can be produced by reacting decanedioic acid with sulfur dichloride oxide, $SOCl_2$. The co-products of the reaction are hydrogen chloride and sulfur dioxide.

Complete the equation for this reaction. [1]

$HOOC(CH_2)_8COOH$ + 2 $SOCl_2$ ⟶ $ClOC(CH_2)_8COCl$ + 2HCl + $2SO_2$

(iii) Draw the repeating unit of nylon 6,10. [1]

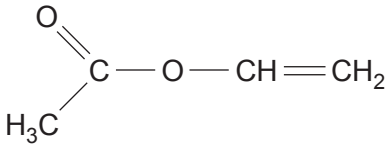


(iv) Nylon 6,10 is described as a condensation polymer.

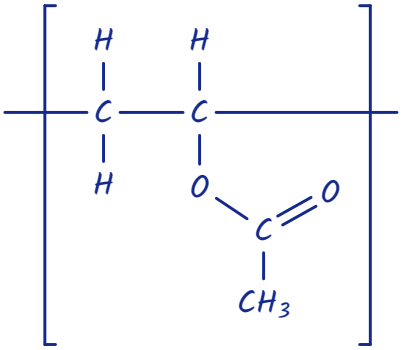
Give the meaning of condensation in this context. [1]

A small molecule, HCl, is lost when each pair of monomers joins (forming an amide link).

(c) Ethenyl ethanoate is the starting material for the manufacture of the addition polymer PVA, which is the main constituent of wood glue.



Draw the repeating unit of PVA. [1]



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(d) The formula of the polymer poly(ethenylnitrate) is $[CH_2CH(ONO_2)]_n$.

It is used in the explosives industry. Combustion of this solid polymer gives carbon dioxide, nitrogen and water.

(i) Balance the equation for this combustion.

For simplicity the formula of poly(ethenylnitrate) is given as $CH_2CH(ONO_2)$. [1]

2 $CH_2CH(ONO_2)(s)$ + 5/2 $O_2(g)$ ⟶ 4 $CO_2(g)$ + $N_2(g)$ + 3 $H_2O(l)$

(ii) Use your equation in part (i) above to calculate the increase in gas volume, measured in dm^3, that occurs when 1 mol of solid $CH_2CH(ONO_2)$ reacts with oxygen.

You should assume that the reaction conditions are 298 K and 1 atm and that water is produced as a liquid. [2]

For 2 mol of solid: gas used = 5/2 = 2.5 mol O_2

gas formed = 4 mol CO_2 + 1 mol N_2 = 5 mol

increase in moles of gas = 5 − 2.5 = 2.5 mol (per 2 mol)

for 1 mol: (2.5 ÷ 2) × 24.5 = 1.25 × 24.5 = 30.6 dm^3

Increase in gas volume = 30.6 dm^3

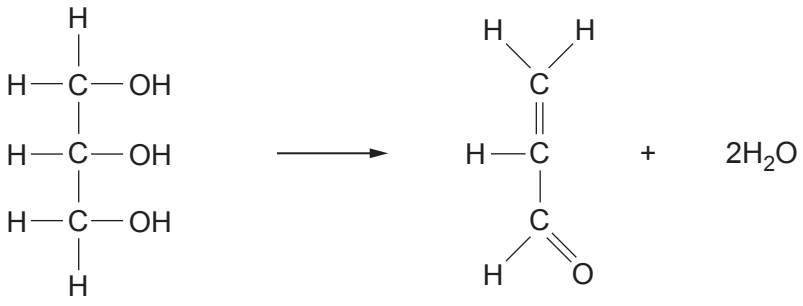
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11. (a) Prop-2-enal can be made by the decomposition of a trihydric alcohol.



M_r 92 M_r 56

(i) Give the systematic name of the trihydric alcohol. [1]

propane-1,2,3-triol

(ii) Suggest the type of reaction that is occurring during the decomposition of this trihydric alcohol. [1]

dehydration

(iii) In an experiment 6.7 g of prop-2-enal was obtained from 0.30 mol of the trihydric alcohol.

Calculate the percentage yield of prop-2-enal. Give your answer to an **appropriate** number of significant figures. [2]

n(prop-2-enal) = 6.7 ÷ 56 = 0.120 mol

mole ratio 1 : 1, so theoretical yield = 0.30 mol

% yield = 0.120 ÷ 0.30 × 100 = 39.9 %

Percentage yield = *39.9* %

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(iv) Calculate the atom economy of this reaction. [1]

total M_r of products = 56 + 2 × 18 = 92 (= M_r of reactant)

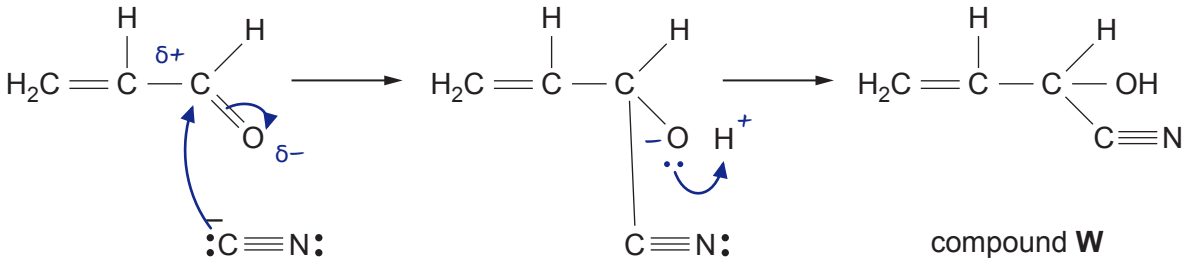
atom economy = 56 ÷ 92 × 100 = 60.9 = 61 %

Atom economy = *61* %

(v) Prop-2-enal reacts with hydrogen cyanide to give compound **W**.

The mechanism for this reaction is similar to the reaction of ethanal and hydrogen cyanide.

I. Complete the mechanism for the reaction. [2]



II. Explain why this mechanism is described as nucleophilic addition. [2]

Initial attack is by the nucleophile CN^- on the $C^{\delta+}$.

HCN adds across the C=O bond (addition).

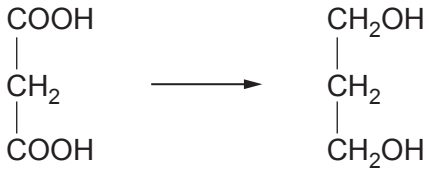
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(b) Propanedioic acid can be used as a starting material in the preparation of certain polyesters.

One stage in this process is the reduction of the acid to propane-1,3-diol.

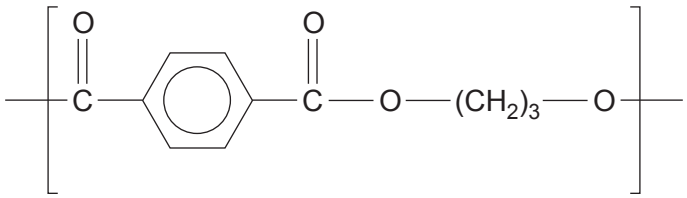


(i) State a reagent that can be used for this reaction. Explain why this process is described as reduction. [2]

Lithium tetrahydridoaluminate(III), $LiAlH_4$ (in dry ether).

Hydrogen is added and oxygen is lost (each COOH becomes CH_2OH).

(ii) The formula for the repeating unit of the polyester PTT is shown below.



State the name of the compound that reacts with propane-1,3-diol to give PTT. [1]

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

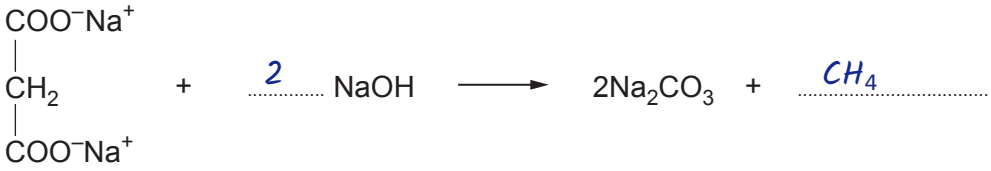
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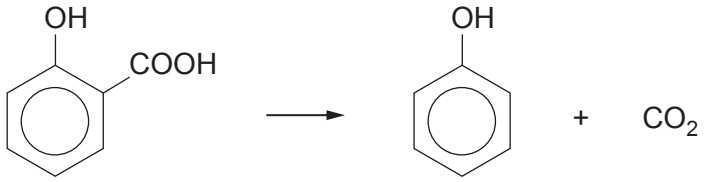
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(c) (i) The process of decarboxylation can be used to reduce the number of carbon atoms in a chain, usually producing an alkane. One method is to heat the sodium salt of the acid with soda lime (shown as NaOH in the equation).

Complete the equation below that shows the decarboxylation of the sodium salt of propanedioic acid. [2]



(ii) If solid 2-hydroxybenzoic acid is slowly heated, decarboxylation occurs, giving phenol.



At intervals during this reaction, samples were removed and dissolved in water.

State a reagent that you could add to the solution to show when decarboxylation was complete. Give the observation and explain your answer. [3]

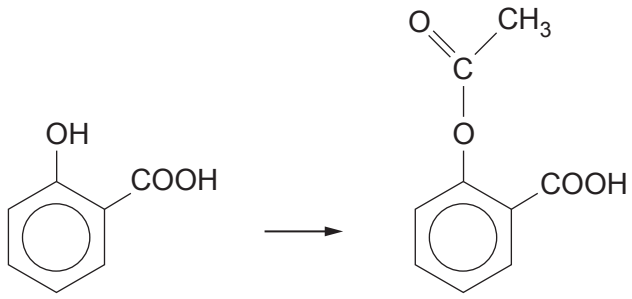
Add sodium hydrogencarbonate, $NaHCO_3(aq)$: reaction is complete when no more effervescence is seen, as the acid gives CO_2 but phenol does not react with $NaHCO_3$.

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(iii) Aspirin is produced from 2-hydroxybenzoic acid by ethanoylation.



At intervals during the reaction, a few drops of the reaction mixture were added to aqueous iron(III) chloride solution.

State how you would know when the reaction was complete. [1]

No purple coloration is seen with the iron(III) chloride, showing that no phenol OH group remains.

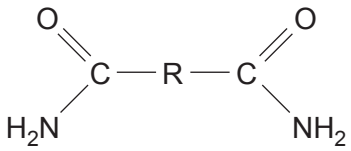
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12. (a) You are provided with a sample of a diamide, where R is an alkyl group.



6.32 g of the diamide reacts with aqueous sodium hydroxide to produce ammonia, which is just neutralised by 32.0 cm^3 of 1.25 mol dm^{-3} sulfuric acid.

The ^1H NMR spectrum of the R group shows a quartet and a triplet in a peak area ratio of 2 : 3.

Use this information to deduce a structure for the diamide.

Your answer should include relevant equations. [6 QER]

$n(H_2SO_4) = 32.0 \div 1000 \times 1.25 = 0.0400$ mol

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$, so $n(NH_3) = 0.0800$ mol

$H_2NCORCONH_2 + 2NaOH \rightarrow NaOOCRCOONa + 2NH_3$

So mole ratio diamide : H_2SO_4 = 1 : 1 and n(diamide) = 0.0400 mol.

M_r of diamide = $6.32 \div 0.0400 = 158$

M_r of R = $158 - 2 \times 44$ ($2 \times CONH_2$) = 70, so R is C_5H_{10}.

The R group has only two proton environments: the quartet is CH_2 next to CH_3 and the triplet is CH_3 next to CH_2, so R contains ethyl groups; area ratio 2 : 3 = 4 H : 6 H, so two CH_2CH_3 groups bonded to a central carbon with no H: $C(CH_2CH_3)_2$.

The diamide is $H_2NCOC(CH_2CH_3)_2CONH_2$ (2,2-diethylpropanediamide).

Check: $C_7H_{14}N_2O_2$, $M_r = 7(12) + 14(1) + 2(14) + 2(16) = 158$.

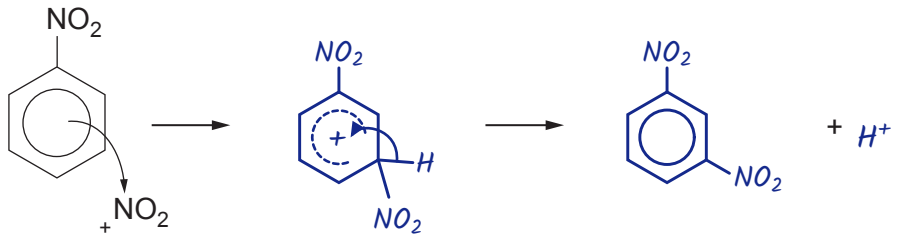
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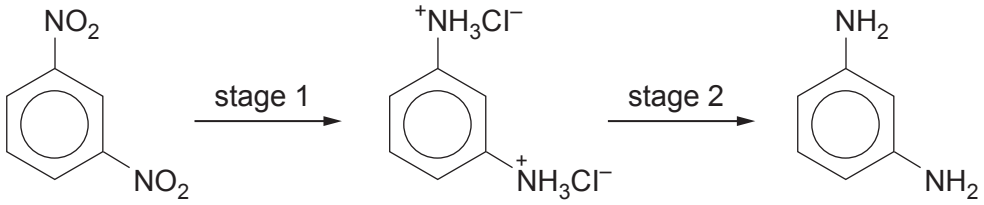
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(b) When benzene is nitrated to form nitrobenzene, some dinitration to form 1,3-dinitrobenzene can occur if the temperature of the reaction rises too high.

(i) Starting from nitrobenzene, complete the mechanism for the formation of 1,3-dinitrobenzene. [2]



(ii) Benzene-1,3-diamine can be obtained by the reduction of 1,3-dinitrobenzene.



I. State the reagent(s) used in stage 1. [1]

tin (Sn) and (concentrated) hydrochloric acid

II. State the reagent(s) used in stage 2. [1]

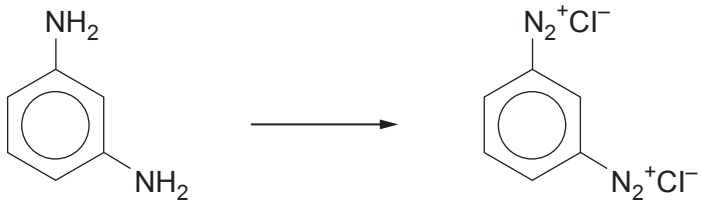
sodium hydroxide, NaOH(aq)

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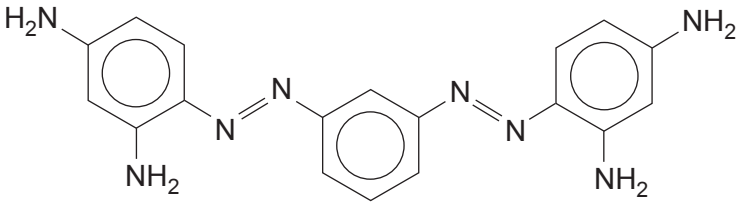
(iii) State the reagent(s) and conditions for the formation of a diazonium compound from benzene-1,3-diamine. [2]



Reagent(s) $NaNO_2$ and HCl (nitric(III) acid, HNO_2)

Conditions 0 to 10 °C (ice bath)

(iv) The diazonium compound formed in part (iii) can react with more unreacted benzene-1,3-diamine to give the azo dye Bismarck brown Y.



This dye is used as a biological stain and is sold for this purpose as a salt, produced from the dye and hydrochloric acid.

Explain how this salt is formed. [1]

The amine (NH_2) groups in the dye have a lone pair on the nitrogen atom, which accepts a proton (H^+) from HCl, forming $NH_3^+Cl^-$.

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(c) Dissolving a solute in a solvent produces a solution that has a lower freezing temperature than the pure solvent.

(i) 0.800 g of ethanoic acid was dissolved in 150 g of benzene.

The resulting solution froze at a temperature 0.222 K lower than that of pure benzene.

Use the equation below to calculate the **apparent** molar mass of ethanoic acid in the benzene solution. [1]

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

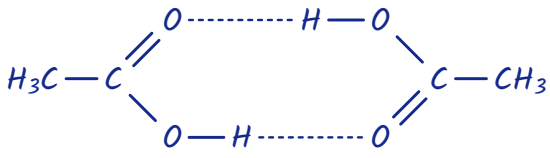
where
K has a numerical value of 5
w is mass of solute
W is mass of solvent
ΔT is depression of freezing temperature

$M_r = (5 \times 1000 \times 0.800) \div (0.222 \times 150)$

$= 4000 \div 33.3 = 120.1$

Molar mass = 120 g mol^{-1}

(ii) Use the **actual** molar mass of ethanoic acid and your answer to part (i) to suggest a possible arrangement for ethanoic acid when it is dissolved in benzene. Give your reasoning. [2]



Actual M_r of ethanoic acid is 60 (half of 120), so in benzene it is present as dimeric molecules held by two hydrogen bonds (above).

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