Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL

A410U20-1

S19-A410U20-1

TUESDAY, 11 JUNE 2019 – 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 7.**	**15**	
Section B	**8.**	**21**	
	9.	**17**	
	10.	**18**	
	11.	**15**	
	12.	**17**	
	13.	**17**	
	Total	**120**	

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ADDITIONAL MATERIALS

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

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

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

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (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.9***(a)* and **Q.12***(a)*.

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

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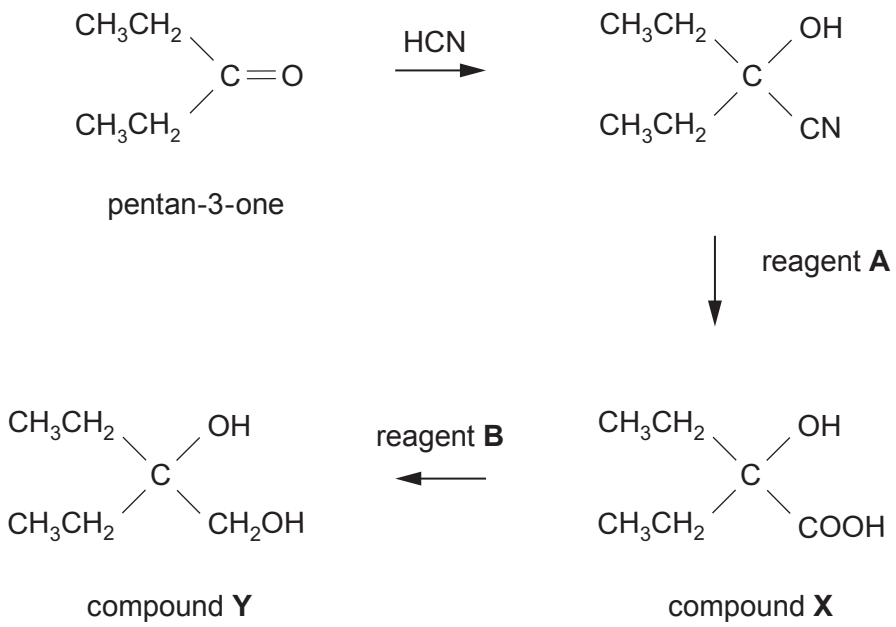
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SECTION A

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

1. Compound **Y** can be made by the following method.



(a) State the type of reaction mechanism taking place when hydrogen cyanide reacts with pentan-3-one. [1]

nucleophilic addition

(b) State the name of reagent **A**. [1]

dilute hydrochloric acid (dilute HCl), heat

(c) Give the empirical formula of compound **X**. [1]

C_2H_4O

(d) Identify reagent **B**. [1]

lithium tetrahydridoaluminate(III), $LiAlH_4$ (in dry ether)

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2. *N*-(phenylazo)phenylamine, $C_6H_5—N{=}N—NH—C_6H_5$, is prepared by reacting benzenediazonium chloride and phenylamine.

(a) State the reagents and conditions needed to prepare a solution of benzenediazonium chloride from phenylamine. [2]

Sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl), i.e. nitrous acid, HNO_2.

Keep the temperature at or below 10 °C (in an ice bath).

(b) In white light *N*-(phenylazo)phenylamine is seen as a yellow solid.

Explain why this compound is yellow in white light. [1]

It absorbs the other colours of white light (the blue end of the visible spectrum)

and reflects (transmits) yellow light, which is the colour we see.

3. An aqueous solution contains sodium benzoate, $C_6H_5COO^-Na^+$, and benzamide, $C_6H_5CONH_2$.

A student was asked to suggest a simple chemical method to produce a solution containing only sodium benzoate and water. He said that he would heat the mixture with aqueous sodium hydroxide.

Explain why this suggestion is correct. [1]

Benzamide is hydrolysed by the hot NaOH(aq) giving sodium benzoate and

ammonia (gas), which is driven off, so only sodium benzoate and water remain.

4. A colourless solution contains either benzoic acid or 2-hydroxybenzaldehyde, $C_6H_4(OH)CHO$.

State **two** chemical tests, apart from using indicator paper, which can be used to identify which compound is present. [2]

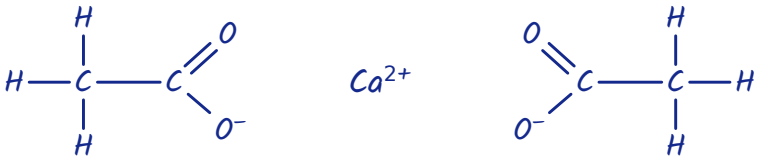
	Reagent(s) used	Result with benzoic acid	Result with 2-hydroxybenzaldehyde
Test 1	$Na_2CO_3(aq)$	effervescence (CO_2 given off)	no reaction
Test 2	Tollens' reagent, warm	no reaction	silver mirror

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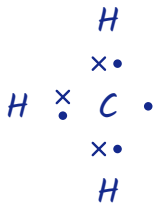
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5. Draw the **displayed** formula of the ionic compound calcium ethanoate, $(CH_3COO)_2Ca$. [1]

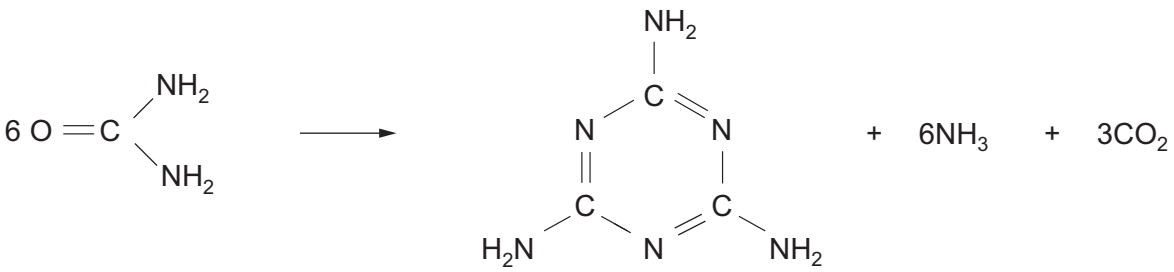


6. Draw a dot and cross diagram of the methyl radical. [1]



(· = C electron, x = H electron; unpaired electron on C)

7. Melamine is made by heating urea.



(a) Calculate the atom economy of this reaction. [2]

M_r urea, $CO(NH_2)_2$ = 60.0; M_r melamine, $C_3H_6N_6$ = 126.0

atom economy = (126 × 100) ÷ (6 × 60) = 12600 ÷ 360 = 35.0 %

Atom economy = 35 %

(b) There have been a number of instances of the illegal addition of melamine to baby milk. This addition appears to increase the percentage of protein in the milk, by increasing its nitrogen content.

Calculate the percentage of nitrogen by mass in melamine. [1]

% N = (6 × 14.0 = 84) ÷ 126 × 100 = 66.7 %

Percentage = 66.7 %

15

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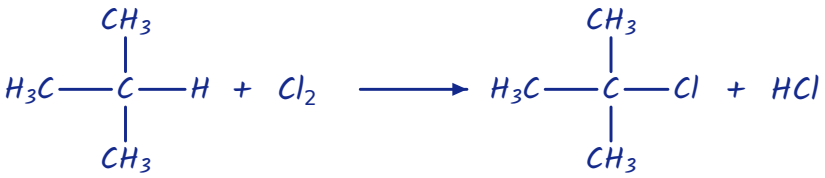
SECTION B

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

8. *(a)* Alkanes react with chlorine to give chloroalkanes.

(i) Give the equation for the reaction of methylpropane, $(CH_3)_3CH$, with chlorine, giving 2-chloro-2-methylpropane as one of the products.

Your answer should show the structures of the reactants and products. [1]



(ii) The chlorination of methylpropane also produces a number of polychlorinated alkanes.

State how these polychlorinated products are formed. [1]

A chlorine radical attacks (removes H from) a chloroalkane already formed,

so further substitution gives polychlorinated products.

(iii) The formula of methylpropane shows that 9 of the 10 hydrogen atoms are equivalent and therefore there is a greater chance of 1-chloro-2-methylpropane being the principal organic product in the first stage of the chlorination reaction.

However, the main product of this chlorination is 2-chloro-2-methylpropane. Suggest a reason for this compound being the main product. [1]

Removing the H from the central carbon gives the tertiary radical $(CH_3)_3C\cdot$,

which is more stable than the primary radical, so the activation energy is

lower and 2-chloro-2-methylpropane forms faster.

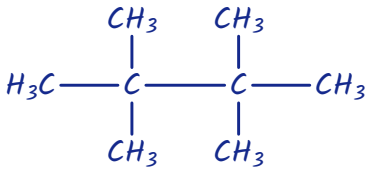
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(iv) Another product of this reaction is a hydrocarbon of molecular formula C_8H_{18}, whose high resolution ^1H NMR spectrum shows only a singlet at 0.86 ppm.

Suggest a structure for this hydrocarbon, explaining why the spectrum shows a singlet. [2]



2,2,3,3-tetramethylbutane

All 18 H atoms are equivalent (six identical CH_3 groups), so one peak; no H is on an adjacent C, so no splitting: a singlet.

(v) Methylpropane is replacing CFCs as a domestic refrigerant. While this material is seen as more environmentally friendly, it is very flammable.

Give the equation for the complete combustion of methylpropane. [1]

$(CH_3)_3CH + 6\frac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O$

(b) Halogenated alkanes cause environmental problems in the ozone layer by their interaction with UV radiation.

Complete the equation below, which shows the effect of UV radiation on chlorofluoromethane. Explain why these products are formed. [2]

$CH_2ClF \longrightarrow \cdot Cl + \cdot CH_2F$

UV causes homolytic fission of the C–Cl bond, because C–Cl is the weakest bond in the molecule (weaker than C–H and C–F), so only C–Cl breaks, giving two radicals.

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(c) Methane clathrate is the name given to methane trapped inside ice crystals. The permafrost contains extensive quantities of this material and there are worries that global warming may lead to the uncontrolled emission of vast quantities of methane.

Use the information below to show that the mole ratio of methane to water (ice) in methane clathrate is about 1 : 5.8.

You should assume that methane clathrate is a material consisting of only methane and ice. [4]

- 1 dm^3 of methane clathrate gives 168 dm^3 of methane measured at 273 K and 1 atm pressure
- 1 dm^3 of methane clathrate has a mass of 900 g

1 mol of gas occupies 22.4 dm^3 at 273 K and 1 atm

$n(CH_4) = 168 \div 22.4 = 7.50$ mol

mass of $CH_4 = 7.50 \times 16.0 = 120$ g

mass of ice = 900 − 120 = 780 g

$n(H_2O) = 780 \div 18.0 = 43.3$ mol

$CH_4 : H_2O = 7.50 : 43.3 = 1 : 5.78$, which is about 1 : 5.8

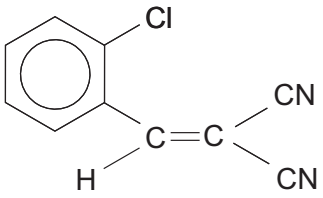
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(d) CS gas (actually a solid) is a substance used to quell social unrest.



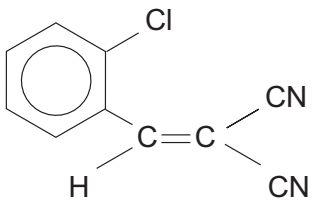
(i) The disposal of surplus stocks of CS gas is a problem which is causing concern. One way is by incineration.

CS gas —(high temperature)→ chlorinated hydrocarbons, hydrogen cyanide gas, polycyclic aromatic hydrocarbons

Suggest **one** reason why this method is seen as an unsatisfactory method of disposal. [1]

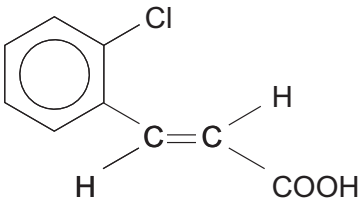
The products are toxic: hydrogen cyanide is a poisonous gas and chlorinated hydrocarbons and polycyclic aromatic hydrocarbons are harmful pollutants. It also needs a high temperature (lots of energy).

(ii) Another method of disposal is by the conversion of CS gas to (2-chlorophenyl)ethene, ammonium sulfate, carbon dioxide and other products.



M_r 189

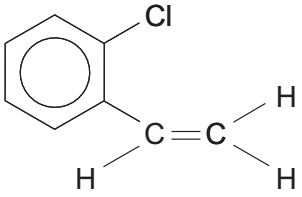
stage 1 →



+ CO_2 + $(NH_4)_2SO_4$

compound **P**

stage 2 ↓ heat with sodalime



+ Na_2CO_3 + H_2O

M_r 139

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I. Stage 1 is an example of a **hydrolysis** reaction.

State what is meant by this term. [1]

A reaction in which a compound is broken down (decomposed) by reaction with water.

II. If stage 1 were carried out in the laboratory a mixture would be obtained, containing ammonium sulfate in solution, together with a precipitate of the organic acid.

State how you would obtain pure crystals of the acid from this mixture. [1]

Filter off the solid acid, wash it with cold water and dry it (recrystallise from a hot solvent if needed).

III. The melting temperature of compound **P** is 209 °C.

State how this figure would change if a sample of compound **P** were impure. [1]

The melting temperature would be lower than 209 °C and the sample would melt over a range of temperatures.

IV. State the type of reaction occurring in stage 2. [1]

decarboxylation

V. The yield of compound **P** in stage 1 was 90.0 % and when compound **P** was converted to (2-chlorophenyl)ethene in stage 2 the yield was 50.0 %.

Calculate the **overall** percentage yield and use your answer to calculate the mass of (2-chlorophenyl)ethene obtained if 75.0 kg of CS gas were destroyed in this way.

Give your answer to an **appropriate** number of significant figures. [4]

overall yield = 0.900 × 0.500 × 100 = 45.0 %

n(CS gas) = 75.0 × 10^3 g ÷ 189 = 396.8 mol

n((2-chlorophenyl)ethene) = 396.8 × 0.450 = 178.6 mol

mass = 178.6 × 139 = 24 820 g = 24.8 kg (3 sig figs)

Mass = 24.8 kg

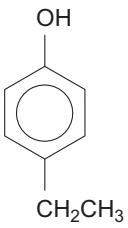
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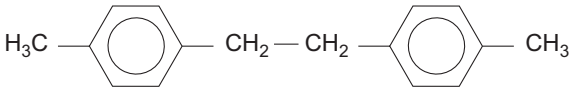
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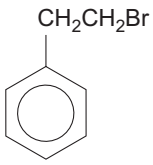
9. *(a)* An unknown compound is one of the six compounds whose structures are shown below.



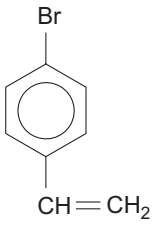
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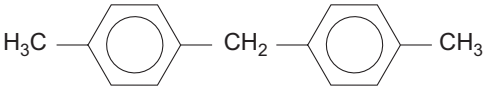
B



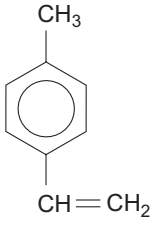
C



D



E



F

Show how you could use infrared spectroscopy to identify **four** of these compounds. In your answer you should state the bonds identified and their absorption values.

For the remaining **two** compounds discuss how high resolution ^{1}H NMR spectroscopy could be used to find the structure of the unknown compound. Your answer should include comments about the splitting pattern seen in the spectra. [6 QER]

IR: only A has an O–H bond: broad peak at 3200 to 3500 cm^{-1}.

D has both a C–Br bond (500 to 600 cm^{-1}) and a C=C bond (1620 to 1670 cm^{-1}).

C has a C–Br absorption at 500 to 600 cm^{-1} but no C=C absorption at 1620 to 1670 cm^{-1}.

F has a C=C absorption at 1620 to 1670 cm^{-1} but no C–Br absorption at 500 to 600 cm^{-1}.

B and E have no O–H, C=C or C–Br bonds, so IR cannot distinguish them.

^{1}H NMR: B and E both show aromatic H peaks at 6.5 to 8.0 ppm. Their CH_3 and CH_2 protons have no H on the adjacent C atom, so each gives a singlet (n + 1 rule, n = 0).

B gives two singlets, CH_3 : CH_2CH_2 in the area ratio 6 : 4 (3 : 2); E gives two singlets, CH_3 : CH_2 in the ratio 6 : 2 (3 : 1).

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(b) Compound **L** is an aromatic compound of formula $C_8H_8Br_2$ (M_r 264).

A sample of compound **L** of mass 3.22 g was refluxed with excess aqueous sodium hydroxide and the resulting mixture acidified with nitric acid. On adding aqueous silver nitrate to this mixture 1.22×10^{-2} mol of silver bromide was obtained.

Use this information to suggest a structure for compound **L**. Explain your answer. [4]

$n(L) = 3.22 \div 264 = 1.22 \times 10^{-2}$ mol

$n(AgBr) = 1.22 \times 10^{-2}$ mol

so L : Br^- released = 1 : 1

only one Br atom is removed



The Br removed must be bonded to an aliphatic (side-chain) carbon, which is hydrolysed by NaOH(aq) to give Br^-; the other Br must be bonded directly to the benzene ring, as the aryl C–Br bond is not hydrolysed. So L is e.g. 1-bromo-4-(2-bromoethyl)benzene (drawn above).

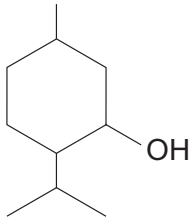
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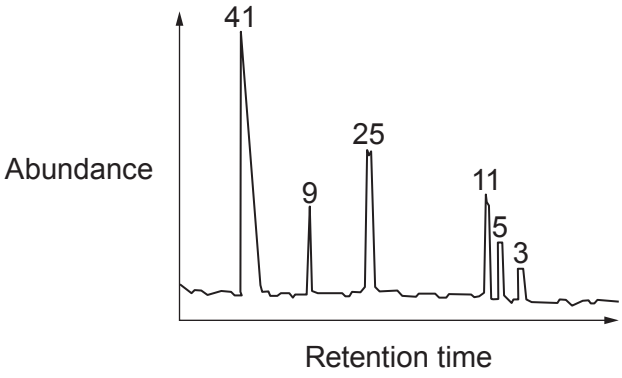
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(c) Menthol, $C_{10}H_{20}O$, is a natural product that has important medicinal uses.



(i) Menthol can be isolated from peppermint oil. Analysis of this oil shows that its major component is menthol. It contains smaller quantities of other compounds. A simplified gas chromatogram of peppermint oil (showing relative peak areas) is shown below.



I. Calculate the percentage by volume of menthol in the oil. [1]

total peak area = 41 + 9 + 25 + 11 + 5 + 3 = 94

% menthol = 41 ÷ 94 × 100 = 43.6

Percentage = *43.6* %

II. The peak of relative area 5 is given by limonene. Limonene is a non-cyclic hydrocarbon whose mass spectrum shows a molecular ion (m/z) at 136.

Use this information to suggest a molecular formula for limonene.
Explain why limonene must be an unsaturated compound. [2]

An alkane would be C_9H_{20} (M_r 128) or $C_{10}H_{22}$ (M_r 142), which do not fit 136. $C_{10}H_{16}$ (136) has fewer H atoms than C_nH_{2n+2} and limonene is non-cyclic, so it must contain C=C.

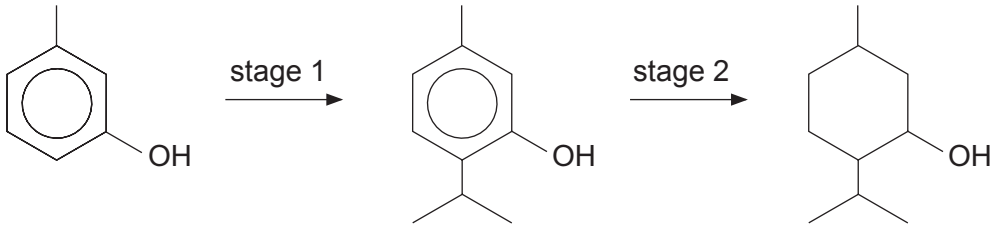
Molecular formula *$C_{10}H_{16}$*

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(ii) One method for producing menthol is shown below.



menthol

I. Give the systematic name for the starting material. [1]

3-methylphenol

II. Stage 1 is the Friedel-Crafts alkylation of the starting material.

Give the names of the reagent and the catalyst used in this stage. [1]

Reagent 2-chloropropane

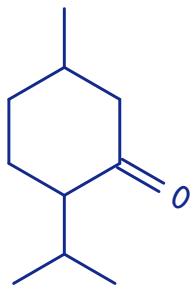
Catalyst aluminium chloride, $AlCl_3$

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

reduction (hydrogenation: addition of H_2)

(iii) Menthol is a secondary alcohol.

Suggest the **skeletal** formula of menthane, $C_{10}H_{18}O$, which is formed by the oxidation of menthol. [1]



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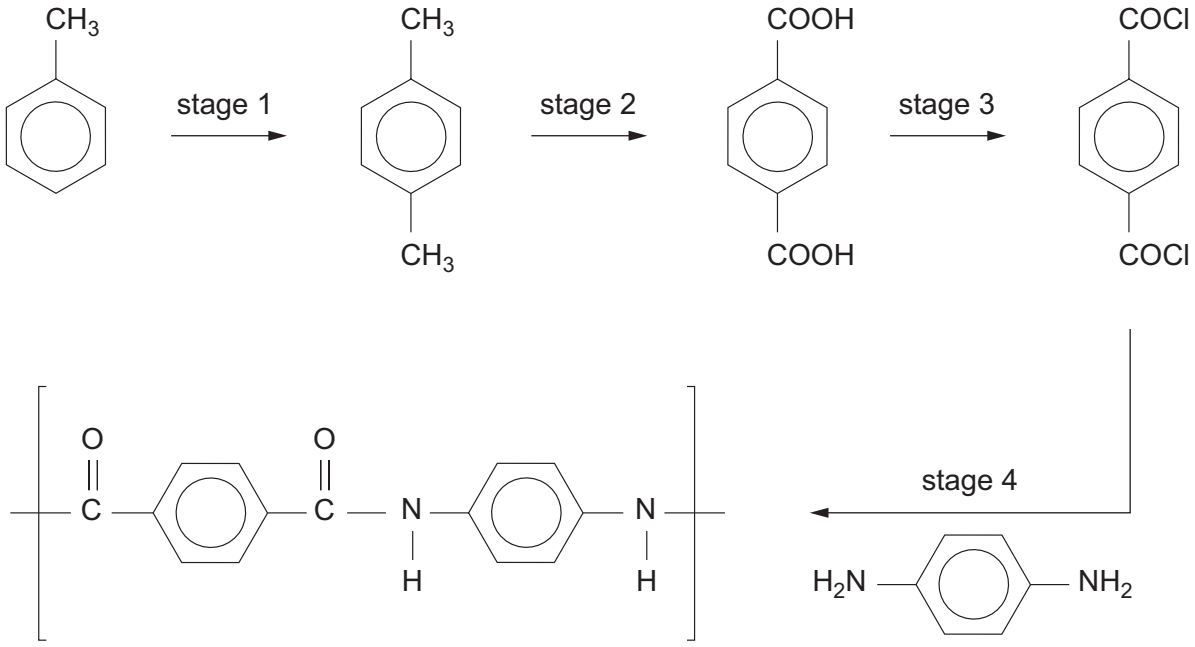
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Turn over.

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10. *(a)* A student was asked to propose a synthesis for the polyamide Kevlar®, starting from methylbenzene. He suggested the following sequence of reactions.



Kevlar®

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

electrophilic substitution

(ii) Suggest why the yield of 1,4-dimethylbenzene in stage 1 will be considerably less than 100%. Problems with the method should not be considered as part of the answer. [1]

Substitution also occurs at other positions on the ring (giving the 1,2-isomer) and polysubstitution can occur.

(iii) State the reagent(s) needed to convert 1,4-dimethylbenzene to benzene-1,4-dicarboxylic acid in Stage 2. [1]

alkaline potassium manganate(VII), $KMnO_4/OH^-$, heat (then acidify)

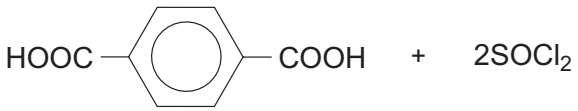
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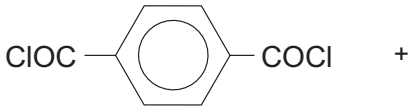
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(iv) In stage 3 the dicarboxylic acid is converted to the acid dichloride.
The student found that the preferred reagent for this reaction was sulfur dichloride oxide, $SOCl_2$.

I. Complete the equation for this reaction. [1]





+ $2SO_2$ + $2HCl$

II. The conversion to the acid dichloride can also be carried out using PCl_3 or PCl_5.

Suggest why the preferred reagent for this reaction is $SOCl_2$. [1]

The other products (SO_2 and HCl) are gases, so they escape and the acid dichloride is easily separated (pure).

III. Suggest why ethanol should not be used as a solvent for this reaction. [1]

$SOCl_2$ would react with the ethanol (rather than with the acid).

(v) In Stage 4 Kevlar® is produced.

State why this polymer is described as a polyamide. [1]

The monomer units are joined by amide linkages, –CO–NH– (C=O bonded to N–H).

(vi) Benzene-1,4-diamine, $C_6H_4(NH_2)_2$, used in stage 4, can be converted to benzene-1,4-diol, $C_6H_4(OH)_2$.

Suggest a reagent(s) that can be used for this reaction. [1]

$NaNO_2$ and HCl (nitrous acid, HNO_2), then warm

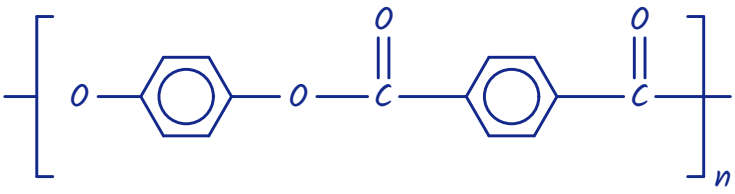
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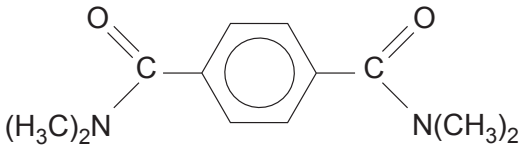
(vii) The student suggested that benzene-1,4-diol can react with the acid dichloride formed in stage 3 to give a different polymer.

Suggest a formula for this polymer, showing a repeating section. [1]



(a polyester)

(viii) While researching a method for making Kevlar®, the student came across the compound below.



I. Describe the **low** resolution ^{1}H NMR spectrum of this compound. Relative peak areas are required in your answer but **not** the position of each signal. [2]

Two peaks: the CH_3 protons and the aromatic (ring) protons, in the area ratio 12 : 4 (3 : 1).

II. Describe the ^{13}C NMR spectrum of this compound identifying the carbon atoms involved. The position of the signals is **not** required. [2]

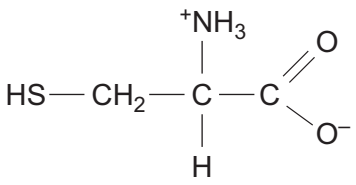
Four peaks (four carbon environments): the CH_3 carbons, the C=O carbons, the aromatic C–H carbons and the aromatic carbons bonded to the aliphatic C=O carbon.

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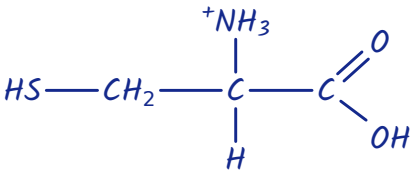
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(b) (i) At pH 5.1 the *α*-amino acid cysteine exists as the zwitterion.



Write the structure of the organic species present when cysteine is added to an aqueous solution of pH 1.0. [1]



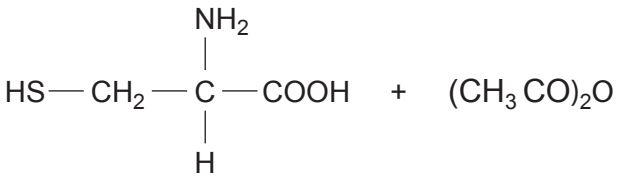
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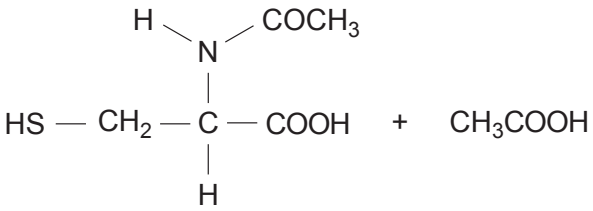
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(ii) *N*-ethanoylcysteine is used to treat an overdose of paracetamol.
It can be produced by the reaction of cysteine with ethanoic anhydride.



cysteine

M_r 121



N-ethanoylcysteine

M_r 163

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In an experiment 0.250 mol of cysteine reacts in a 1 : 1 ratio with ethanoic anhydride.

I. Ethanoic anhydride has a density of 1.08 g cm^{-3}.

Calculate the volume of ethanoic anhydride needed. [2]

M_r $(CH_3CO)_2O$ = 102.0; mass = 0.250 × 102.0 = 25.5 g

volume = mass ÷ density = 25.5 ÷ 1.08 = 23.6 cm^3

Volume = 23.6 cm^3

II. After the reaction a 90 % yield of *N*-ethanoylcysteine is formed.

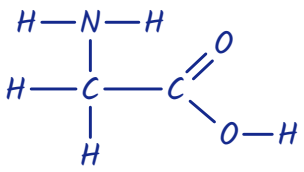
Calculate the mass of *N*-ethanoylcysteine formed. [1]

mass = 0.250 × 0.90 × 163 = 36.7 g

Mass = 36.7 g

(iii) Cysteine is an *α*-amino acid that contains a chiral centre.

Write the displayed formula of an *α*-amino acid that does **not** contain a chiral centre. [1]



glycine (two identical H atoms on the α-carbon)

18

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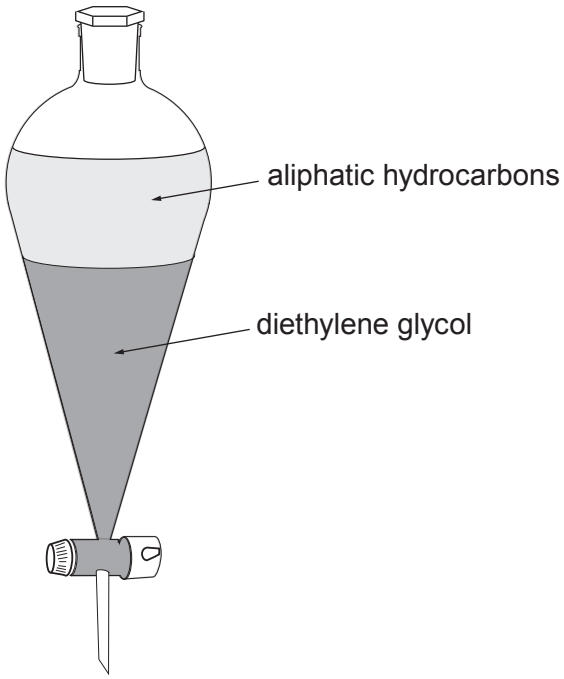
11. *(a)* (i) Naphtha, obtained from crude oil (petroleum) contains hexane.

Write the equation for the conversion (reforming) of hexane into benzene and hydrogen. [1]

$C_6H_{14} \rightarrow C_6H_6 + 4H_2$

(ii) The reforming of naphtha produces a number of other liquid products in addition to benzene.

I. One method of separating benzene from aliphatic products is to use solvent extraction. Benzene dissolves in diethylene glycol whereas aliphatic hydrocarbons are largely insoluble in this solvent. In the laboratory this can be demonstrated using a separating funnel.



Describe the use of a separating funnel containing the two layers shown above, to obtain a separate sample of the diethylene glycol layer. [1]

Remove the stopper, open the tap and run off the lower (diethylene glycol) layer into a beaker, closing the tap as soon as the boundary between the layers reaches the tap.

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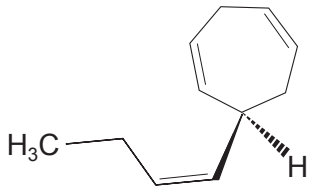
II. The boiling temperatures of benzene and diethylene glycol are 80 °C and 245 °C respectively.

State the name of the technique used to separate these two liquids and state how you could make sure that the risk of fire is reduced to a minimum. [2]

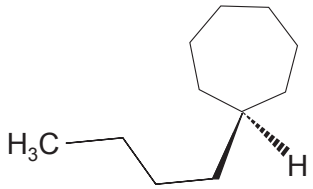
(Simple) distillation: benzene distils off at 80 °C.

Heat using a water bath or an electric heating mantle, not a naked flame.

(b) Ectocarpene is a hydrocarbon produced by certain algae.



(i) 4.31 dm^3 of hydrogen, measured at 312 K and at a pressure of 1.01×10^5 Pa, was needed to completely react with 8.29 g of ectocarpene to produce compound **G**.



compound **G**

Use this information to confirm that the relative molecular mass of ectocarpene is 148. [4]

$n(H_2) = pV \div RT = (1.01 \times 10^5 \times 4.31 \times 10^{-3}) \div (8.31 \times 312) = 0.168$ mol

ectocarpene has three C=C bonds (G has none), so 1 mol reacts with 3 mol H_2

n(ectocarpene) = 0.168 ÷ 3 = 0.0560 mol

M_r = mass ÷ moles = 8.29 ÷ 0.0560 = 148

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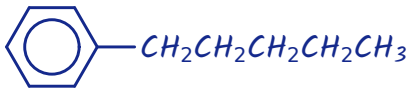
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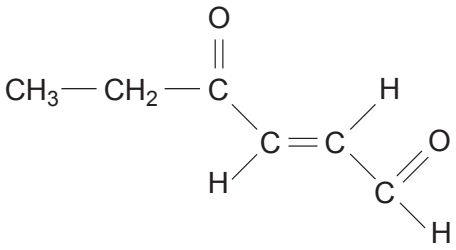
(ii) Find the molecular formula of ectocarpene and deduce the structural formula of an aromatic compound that has the same molecular formula as ectocarpene. [2]

Molecular formula $C_{11}H_{16}$

Structural formula



(c) A particular insect defends itself by producing a mixture of compounds that contains compound **W**.



compound **W**

(i) Give the structure of the compound obtained when compound **W** reacts with sodium tetrahydridoborate(III), $NaBH_4$. [1]

$CH_3CH_2CH(OH)CH=CHCH_2OH$

(ii) Compound **W** is warmed with Tollens' reagent.

Describe what is seen (if anything) and explain your observation. [2]

A silver mirror forms (grey/black solid). W has an aldehyde group (-CHO), which is oxidised and reduces the Ag^+ ions in Tollens' reagent to silver metal, Ag.

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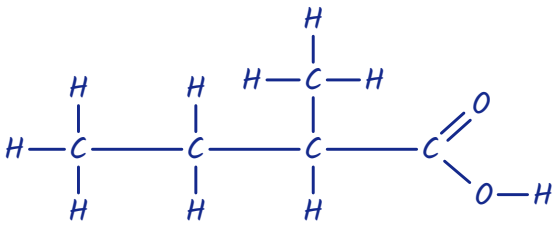
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(d) Another insect produces a defensive mixture that contains 2-methylbutanoic acid.

Write the displayed formula of 2-methylbutanoic acid. Give an isomer of this compound that has only three signals in its ^{13}C NMR spectrum, one of which occurs at 160-185 ppm. [2]

Structure of 2-methylbutanoic acid



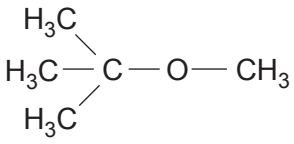
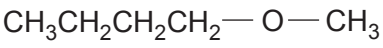
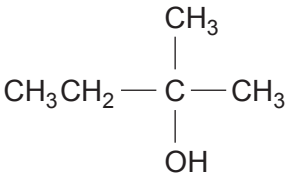
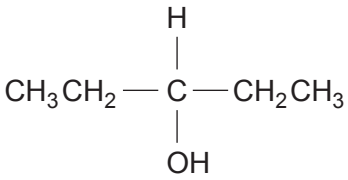
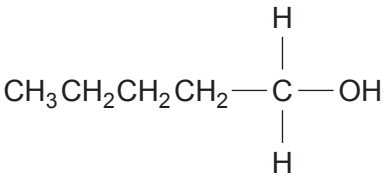
Structure of the isomer

$(CH_3)_3C-COOH$ (2,2-dimethylpropanoic acid)

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12. *(a)* The boiling temperatures of five isomers of formula $C_5H_{12}O$ are shown in the table below.

Compound	Formula	Boiling temperature / °C
A		56
B		71
C		102
D		116
E		137

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Discuss the intermolecular bonding present in these compounds and relate this bonding to the differences observed in their boiling temperatures. [6 QER]

A and B are ethers: with no O–H bond they cannot form hydrogen bonds between molecules; only van der Waals forces (and weak dipole–dipole forces) act.

C, D and E are alcohols: the O–H group forms hydrogen bonds between molecules (δ+ H to a lone pair on δ− O), which are much stronger than van der Waals forces.

More energy is needed to overcome them, so C, D and E (102 to 137 °C) boil higher than A and B (56 and 71 °C).

All are isomers with the same number of electrons, so within each group the difference is due to shape: the more branched the chain, the lower the boiling temperature.

A is highly branched (more spherical), so its molecules pack less well with less surface contact and weaker van der Waals forces than straight-chain B: A boils at 56 °C, B at 71 °C.

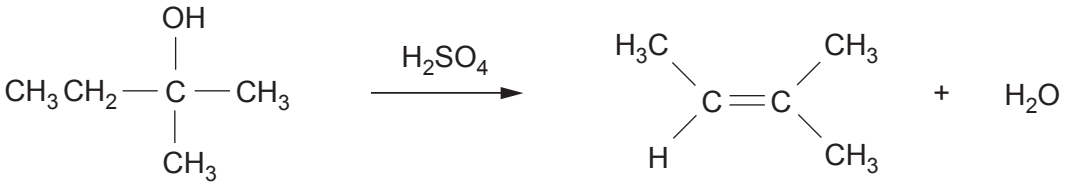
Likewise C, the most branched alcohol, boils lowest (102 °C), then D (116 °C); straight-chain E boils highest (137 °C) as its molecules pack most efficiently, giving the strongest intermolecular forces.

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(b) The equation below shows the reaction of 2-methylbutan-2-ol with sulfuric acid.



(i) State why the sulfuric acid acts as a catalyst in this reaction. [1]

It increases the rate of the reaction (H^+ is used in the first step) but it is regenerated, so it is not used up.

(ii) In the first stage of the mechanism of this reaction, 2-methylbutan-2-ol acts as a base.

Suggest how it can react as a base. [1]

A lone pair on the O atom of the –OH group accepts a proton (H^+) from the acid: it is a lone pair donor / proton acceptor.

(iii) The main organic product of the reaction is 2-methylbut-2-ene but a small percentage of 2-methylbut-1-ene, $CH_3CH_2C(CH_3)=CH_2$ is also produced.

Suggest why this alkene is also a product. [1]

Elimination of water involves loss of the OH and a proton from a carbon atom next to the C–OH carbon. Losing H from the CH_2 gives 2-methylbut-2-ene, but losing H from a CH_3 on that carbon gives 2-methylbut-1-ene.

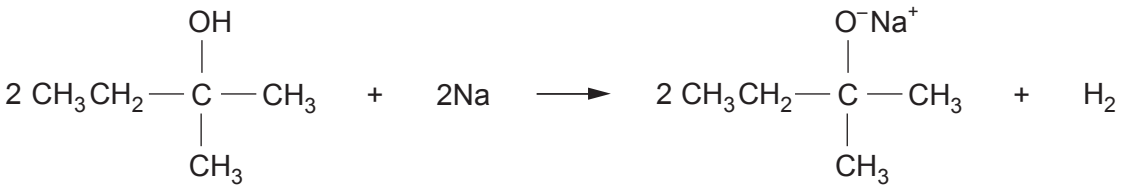
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(iv) The mixture at the end of the reaction contains the two alkenes and a small quantity of unreacted 2-methylbutan-2-ol.

A student found that 2-methylbutan-2-ol reacts with sodium to give hydrogen as one of the products.



A 10.0 g sample of the mixture was reacted with an excess of sodium. This produced 125 cm^3 of hydrogen measured at 298 K and 1 atm pressure.

Calculate the mass of 2-methylbutan-2-ol in the mixture. [2]

only the alcohol reacts with Na (2 mol alcohol give 1 mol H_2)

$n(H_2) = 125 \div 24\,500 = 5.10 \times 10^{-3}$ mol

$n(\text{alcohol}) = 2 \times 5.10 \times 10^{-3} = 1.02 \times 10^{-2}$ mol; M_r $C_5H_{12}O = 88.1$

mass = $1.02 \times 10^{-2} \times 88.1 = 0.899$ g

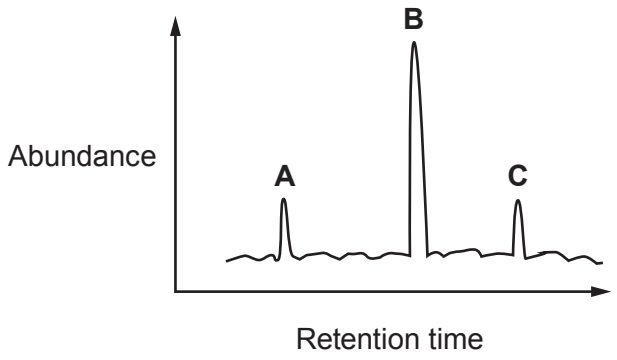
Mass = 0.899 g

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(v) A sample of the product mixture from this reaction produced the following gas chromatogram.



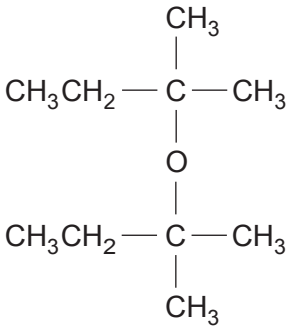
I. State, giving a reason, which of these peaks is given by 2-methylbut-2-ene. [1]

Peak B, because 2-methylbut-2-ene is the major (main) product, so it gives the largest peak.

II. Suggest how you would confirm which one of the remaining two peaks is given by 2-methylbutan-2-ol. [1]

Run a known (pure) sample of 2-methylbutan-2-ol through the same column under the same conditions and compare retention times; or add some 2-methylbutan-2-ol to the mixture and see which peak becomes larger.

(vi) In this reaction the alcohol is added slowly to an excess of sulfuric acid. However, if sulfuric acid is added slowly to the alcohol, then the product below is also formed.



Suggest how this compound can be formed in the reaction. [1]

Two molecules of the alcohol join with the elimination of one molecule of water (condensation) to give the ether.

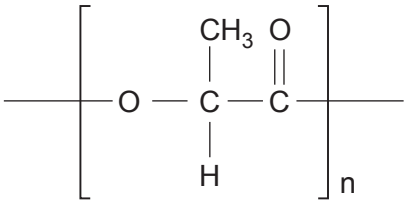
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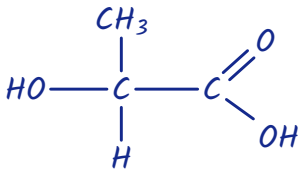
(c) (i) Many polymers persist in the environment for many years and are causing severe pollution problems. There is an increasing use of materials that lead to fewer environmental problems.

Some cardboard drinking cups have an impervious PLA lining. PLA is made from plants and is biodegradable.

The formula of the repeating section of PLA is shown below.



Give the structure of the monomer of PLA. [1]



(2-hydroxypropanoic acid)

(ii) Suggest **two** desirable properties of PLA if it is to be used for lining the cardboard of a cup used for hot drinks. [2]

1. Melting (softening) point well above 100 °C, so it does not soften.

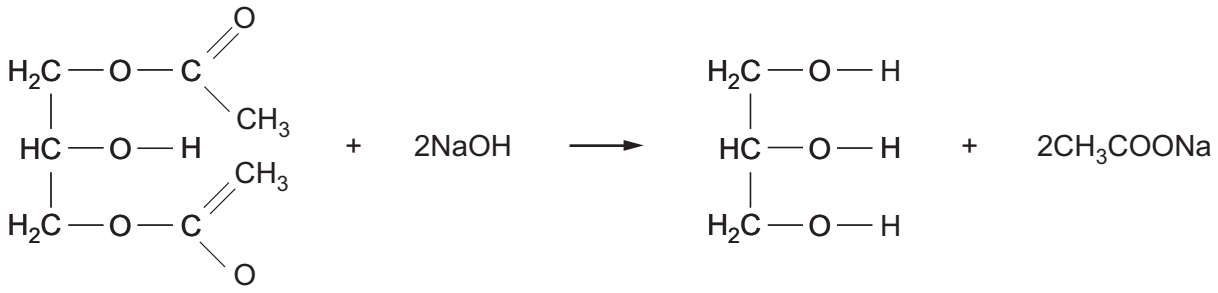
2. Does not react with (is insoluble in) hot water/drinks and is non-toxic.

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13. *(a)* Diacetin is an ester of propane-1,2,3-triol that is used by some plants to attract bees. It reacts with aqueous sodium hydroxide to produce propane-1,2,3-triol and sodium ethanoate.



diacetin

1.58 g of diacetin was heated with 50.0 cm^3 of aqueous sodium hydroxide of concentration 0.500 mol dm^{-3}. After complete reaction with the diacetin 7.00×10^{-3} mol of sodium hydroxide remained.

Use this information to show that the relative molecular mass of diacetin is 176. [4]

n(NaOH) at start = 50.0 × 0.500 ÷ 1000 = 0.0250 mol

n(NaOH) reacted = 0.0250 − 0.00700 = 0.0180 mol

2 mol NaOH react with 1 mol diacetin,

so n(diacetin) = 0.0180 ÷ 2 = 0.00900 mol

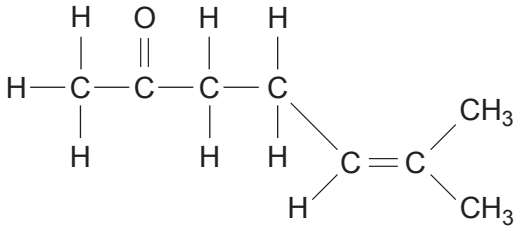
M_r = mass ÷ moles = 1.58 ÷ 0.00900 = 175.6, which is 176

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(b) 2-Methylhept-2-en-6-one acts as an alarm pheromone in certain species of ants.



2-methylhept-2-en-6-one

(i) State why this compound does not show *E*-*Z* isomerism. [1]

One carbon atom of the C=C double bond has two identical groups attached (two CH_3 groups).

(ii) Draw the structure of a ketone with the same molecular formula that **can** exist as *E*-*Z* isomers. [1]

$CH_3COCH_2CH_2CH=CHCH_2CH_3$

(oct-5-en-2-one, $C_8H_{14}O$; each C of C=C has H and a different group)

(iii) 2-Methylhept-2-en-6-one gives a positive triiodomethane test.

State the reagent(s) used for this test and the observation. [2]

Reagent(s) *iodine and aqueous sodium hydroxide (alkaline I_2), warm*

Observation *pale yellow precipitate (of CHI_3)*

(iv) The reaction of 2-methylhept-2-en-6-one with aqueous sodium tetrahydridoborate(III) results in the formation of a new compound which has forms that rotate the plane of plane polarised light.

Give the structure of the compound formed and explain why it has forms that rotate the plane of plane polarised light. [2]

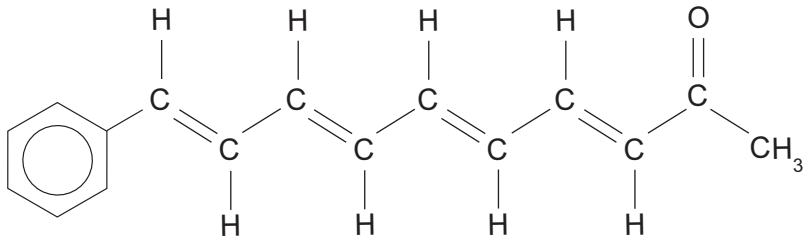
$CH_3C^*H(OH)CH_2CH_2CH=C(CH_3)_2$

C^* is a chiral centre; it has four different groups (H, OH, CH_3 and the C_5 chain), so the molecule is not superimposable on its mirror image and exists as two optical isomers (enantiomers), which rotate the plane of plane polarised light in opposite directions.

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(c) (i) A species of sea slug produces an alarm pheromone which is a mixture of three compounds. One of these compounds is Navenone B.



The visible spectrum of this compound shows an absorption maximum at 377 nm.

Calculate the energy of this absorption in kJ mol^{-1}. [3]

$f = c \div \lambda = 3.00 \times 10^{8} \div 377 \times 10^{-9} = 7.96 \times 10^{14}$ Hz

$E = hf = 6.63 \times 10^{-34} \times 7.96 \times 10^{14} = 5.28 \times 10^{-19}$ J

per mole: $5.28 \times 10^{-19} \times 6.02 \times 10^{23} = 3.18 \times 10^{5}$ J mol^{-1}

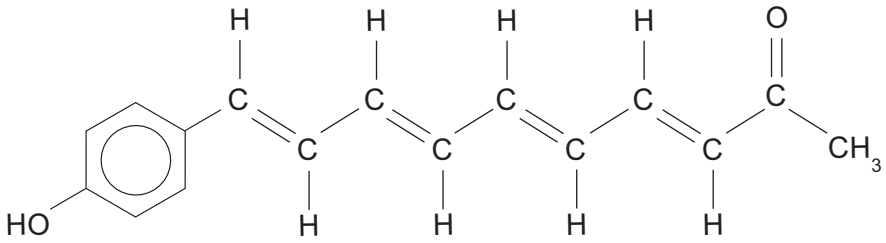
Energy = 318 kJ mol^{-1}

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(ii) Navenone C is a similar compound.



This compound reacts with hydrogen bromide and with bromine.

I. State what is seen when bromine is added to a solution of Navenone C. [2]

The orange (red-brown) bromine is decolourised and a white precipitate forms.

II. State the type of reaction mechanism occurring when Navenone C reacts with hydrogen bromide. [1]

electrophilic addition

III. Complete the table below to show the mole ratios of the added reagent and Navenone C.

The table is already completed for the reaction with bromine. [1]

Reagent added	Mole ratio Added reagent : Navenone C
hydrogen bromide	4 : 1
bromine	6 : 1

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