Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL

A410U20-1

S18-A410U20-1

CHEMISTRY – A level component 2
Organic Chemistry and Analysis

TUESDAY, 12 JUNE 2018 – AFTERNOON

2 hours 30 minutes

	For Examiner's use only		
	Question	Maximum Mark	Mark Awarded
Section A	1. to 9.	15	
Section B	10.	19	
	11.	18	
	12	17	
	13	16	
	14	19	
	15	16	
	Total	120	

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01

ADDITIONAL MATERIALS

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

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

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.11***(a)* and **Q.14***(b)*(ii).

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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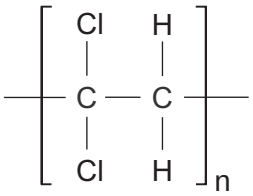
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SECTION A

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

1. Give the **name** of the monomer that is used to produce the polymer shown below. [1]



1,1-dichloroethene

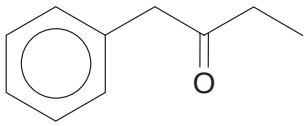
2. Give the structure of a product obtained when 1,4-dimethylbenzene is oxidised by alkaline potassium manganate(VII) and acidified. [1]



benzene-1,4-dicarboxylic acid

3. The compound below is reduced by sodium tetrahydridoborate(III).

State, giving a reason, whether a primary, secondary or tertiary alcohol is produced. [1]



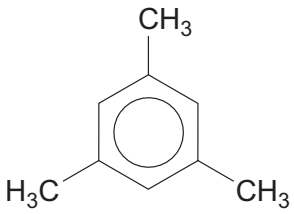
Secondary alcohol, because the compound is a ketone (C=O bonded to two carbon atoms) and ketones are reduced to secondary alcohols.

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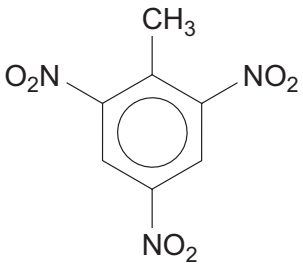
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4. The formulae for two aromatic compounds are given below.



mesitylene



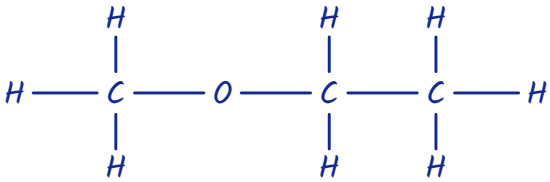
TNT

Complete the table which describes the ^{1}H NMR signals for these two compounds. [2]

Compound	Number of peaks	Relative peak area ratio
mesitylene	2	3 : 1
TNT	2	3 : 2

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5. Draw the structure for a compound of formula C_3H_8O that shows an infrared absorption peak between 1000 and 1300 cm^{-1} but no peak between 2500 and 3550 cm^{-1}, other than that at 2800-3100 cm^{-1} corresponding to C—H bonds. Give your reasoning. [2]



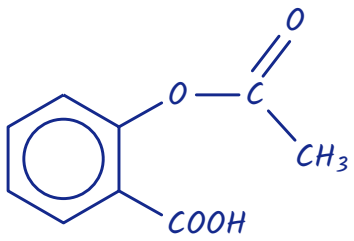
methoxyethane (an ether)

It has a C–O bond (1000 to 1300 cm^{-1}) but no O–H bond (no peak at 2500 to 3550 cm^{-1}), so it cannot be an alcohol.

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6. *(a)* Give the structure of the organic compound produced when 2-hydroxybenzenecarboxylic acid reacts with ethanoyl chloride. [1]



(b) If the product in *(a)* was contaminated with unreacted 2-hydroxybenzenecarboxylic acid, describe a chemical test that would show its presence. State the reagents used and the observation made. [2]

Add neutral aqueous iron(III) chloride solution.

A purple colour forms, showing the phenol (OH) group of unreacted

2-hydroxybenzenecarboxylic acid is present.

7. Benzene-1,2-dicarboxylic acid (or its sodium salt) is heated with sodalime.

State the type of reaction that occurs and give the name of the product. [2]

Type of reaction: decarboxylation.

Product: benzene.

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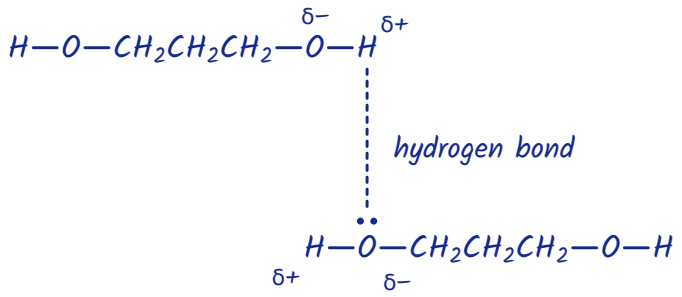
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8. The boiling temperatures of three compounds of formula $C_3H_8O_2$ are given in the table.

Compound		Boiling temperature / °C
L	$CH_3–CH_2–O–O–CH_3$	40
M	$CH_3–O–CH_2–O–CH_3$	42
N	$HO–CH_2–CH_2–CH_2–OH$	214

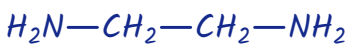
Suggest why the boiling temperature of compound **N** is considerably higher than the boiling temperatures of the other two compounds, illustrating your answer by means of a diagram. [2]



Only N has O–H groups, so N molecules form hydrogen bonds to each other.

These are stronger intermolecular forces than the dipole and van der Waals forces in L and M, so more energy is needed to separate the molecules.

9. Draw the structure of a compound that has an empirical formula CH_4N. [1]



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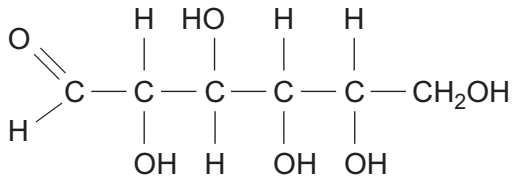
SECTION B

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

10. The willow tree has been used for hundreds of years to obtain substances with medical benefits. One of these substances is salicin, which shows analgesic and anti-inflammatory properties.

Salicin is a molecule that consists of two parts – one based on glucose and the other on (2-hydroxyphenyl)methanol, $C_6H_4(OH)CH_2OH$.

(a) The formula of glucose can be written as an open-chain formula.



Glucose is a reducing sugar and will react with Fehling's reagent.

State what is seen in the test with Fehling's reagent and identify the group present in glucose that is responsible for this reaction. [2]

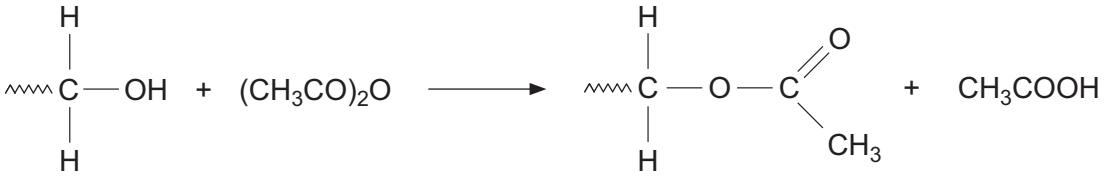
The blue solution gives an orange-brown precipitate.

The aldehyde (CHO) group is responsible.

(b) An outline of the method used to make glucose pentaethanoate is shown below.

- 0.015 mol of glucose is placed in a flask with a large excess of ethanoic anhydride.
- The mixture is heated under reflux at 100 °C for one hour.
- The product is cooled and poured into a beaker containing crushed ice.
- After stirring and allowing the ice to melt, the mixture is filtered.
- Ethanol is then used to recrystallise the glucose pentaethanoate.

(i) In this reaction the —OH groups in glucose react with ethanoic anhydride to give ethanoate groups.



State and explain the minimum number of moles of ethanoic anhydride used in this reaction. [2]

0.075 mol, because glucose has 5 alcohol (OH) groups that each react

1:1 with ethanoic anhydride (5 × 0.015 = 0.075 mol).

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(ii) Briefly outline how the mixture could be 'heated under reflux at 100 °C'. [2]

Heat the flask in a boiling water bath or heating mantle.

Fit a vertical condenser: its cold water jacket condenses the vapours and returns them to the flask.

(iii) State how the method implies that glucose pentaethanoate is insoluble in water. [1]

The product is precipitated as a solid when the mixture is poured into a large excess of water (crushed ice).

(iv) During recrystallisation glucose pentaethanoate is dissolved in the 'minimum quantity of hot ethanol'.

Why was the '**minimum** quantity' used? [1]

So that the hot solution is saturated and the maximum amount of glucose pentaethanoate crystallises out on cooling, with as little as possible left dissolved in the ethanol.

(v) The melting temperature of glucose pentaethanoate is 134 °C. In the experiment the sample is found to melt at a lower temperature.

Suggest a possible cause for this lower value. [2]

A lower melting temperature shows that the compound is impure.

It could be contaminated with unreacted glucose or remaining ethanoic anhydride, or still be damp.

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(c) Ethanol can be made from glucose by fermentation.

$$C_6H_{12}O_6(aq) \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

In an experiment 0.200 mol of glucose was dissolved in water and fermented using yeast. At the end of the reaction all the glucose had been converted into ethanol and carbon dioxide. If the volume of the resulting solution was 2.03 dm^3, calculate the concentration of ethanol in g dm^{-3}. [3]

1 mol glucose gives 2 mol ethanol, so 0.200 mol gives 0.400 mol ethanol

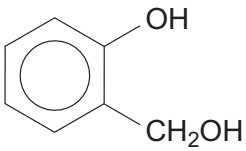
$M_r(C_2H_5OH) = 46.0$

mass of ethanol = $0.400 \times 46.0 = 18.4$ g in 2.03 dm^3

concentration = $18.4 \div 2.03 = 9.06$ g dm^{-3}

Concentration = 9.06 g dm^{-3}

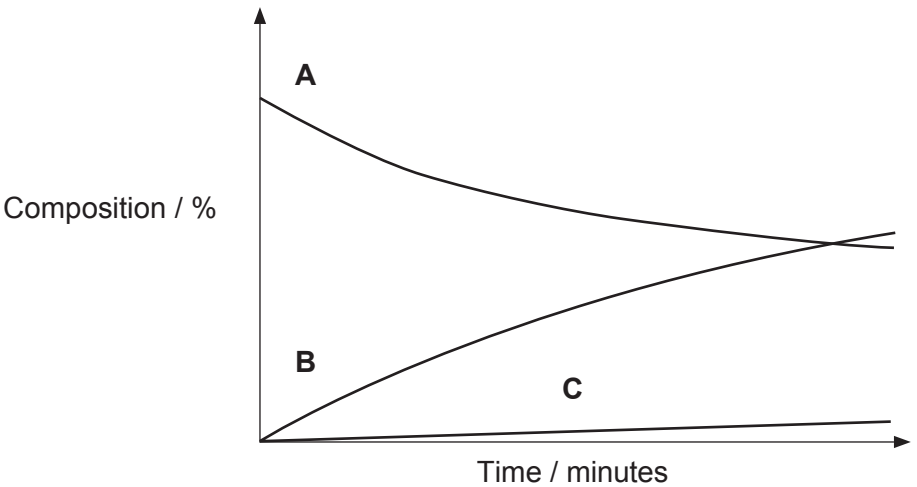
(d) The other product from the breakdown of salicin is (2-hydroxyphenyl)methanol – compound **A** below.



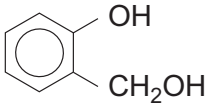
compound **A**

Compound **A** is both a phenol and an alcohol and oxidation of the alcohol group results in a number of other products, including compounds **B** and **C**. Both of these compounds have important commercial uses and a method that gives them in high yields is desirable.

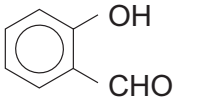
In one method, compound **A** is oxidised at 50 °C using water as the solvent.
The graph shows the composition of the resulting mixture.



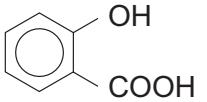
A



B



C



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(i) State how the quantity of compound **A** present in the mixture changes over time. [1]

The amount of A decreases rapidly at the start, then decreases more slowly as the reaction proceeds.

(ii) Comment on the proportion of compounds **B** and **C** in the mixture as the reaction proceeds. [1]

The proportion of B shows a steady rise as time increases, but the proportion of C remains very small and rises only very slowly.

(iii) The proportion of products present was found using HPLC.

Calculate the percentage of compound **A** oxidised after 15 minutes. [1]

	Concentration / mol dm^{-3}	
Compound	Start	After 15 minutes
A	0.20	0.02
B	0.00	0.10
C	0.00	0.01
other products	0.00	0.07

A oxidised = 0.20 − 0.02 = 0.18 mol dm^{-3}

percentage = (0.18 ÷ 0.20) × 100

Percentage oxidised = 90 %

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(iv) Compounds **A**, **B** and **C** are colourless and were detected during HPLC by using ultraviolet radiation.

Absorption maximum / nm	Compound
202.1	**C**
212.2	**B**
273.4	**A**

State, giving a reason, which of these three compounds has the absorption maximum of the highest energy. [2]

Compound C, as it absorbs at the shortest wavelength (202.1 nm).

E = hf and c = fλ, so E = hc/λ: the shortest wavelength has the highest frequency and so the highest energy.

(v) This oxidation can also be carried out using benzene as the solvent.
Compound **B** is the only product and the rate of oxidation is higher than when using water as the solvent.

Give a reason why the method using water is seen as a 'greener' process. [1]

It does not use a toxic solvent like benzene; water does not harm the environment.

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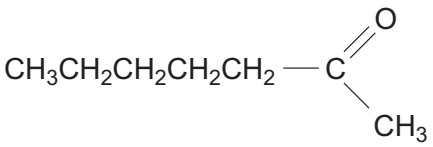
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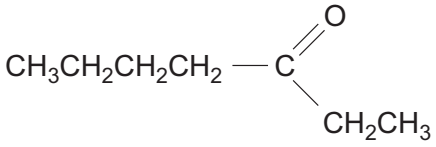
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11. *(a)* The characteristic smell of some varieties of blue cheese is due mainly to heptan-2-one.



heptan-2-one



heptan-3-one

A teacher was asked whether heptan-2-one could be clearly distinguished from heptan-3-one by some suggested methods. His responses are shown in the table.

Method	Clearly identified?
mass spectroscopy	yes
gas-liquid chromatography	no
boiling temperature	yes
chemical analysis for C, H and O	no
reaction with alkaline iodine	yes
reaction with 2,4-dinitrophenylhydrazine	no
reaction with Tollens' reagent	no

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Explain why each response is correct. [6 QER]

Mass spectroscopy (yes): each compound has its own mass spectrum. The molecular ion is the same (m/z 114) but the fragmentation patterns differ, e.g. CH_3CO^+ (m/z 43) from heptan-2-one and $C_2H_5CO^+$ (m/z 57) from heptan-3-one.

GLC (no): the two isomers have the same retention times, so they cannot be told apart.

Boiling temperature (yes): they are different compounds, so their boiling temperatures must be different.

Chemical analysis (no): both have the same molecular formula, $C_7H_{14}O$, so the elemental analysis for C, H and O is the same for each.

Alkaline iodine (yes): only methyl ketones (CH_3CO- group) give a positive test, a pale yellow precipitate of CHI_3, so only heptan-2-one reacts.

2,4-DNPH (no): both ketones give an orange precipitate. To distinguish them the derivatives would need different melting temperatures, but these are very close to each other.

Tollens' reagent (no): neither compound is an aldehyde, so neither is oxidised and no silver mirror is seen with either.

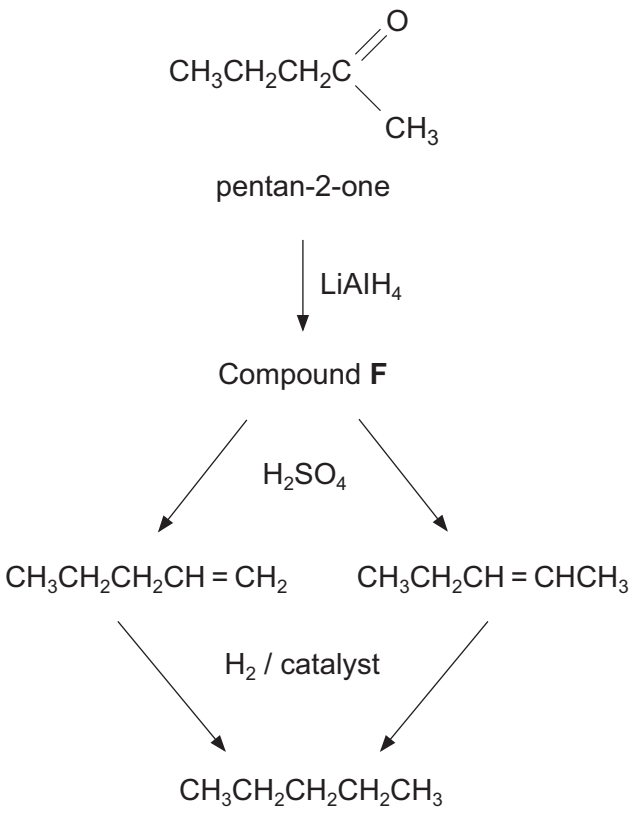
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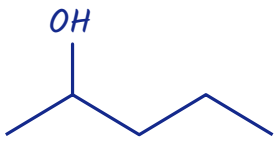
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(b) Pentan-2-one contributes to the smell of other blue cheese varieties.

A reaction sequence for obtaining pentane from pentan-2-one is shown below.



(i) Give the **skeletal** formula of compound **F**. [1]



(ii) State the role of sulfuric acid when it reacts with compound **F** and explain why two products are formed. [2]

Sulfuric acid acts as a dehydrating agent, eliminating water.

Water can be eliminated from either side of the –CH(OH)– group, giving two different alkenes.

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(iii) The final stage involves catalytic hydrogenation. One method of carrying this out is to dissolve the alkene in a suitable solvent and react it with hydrogen at room temperature in the presence of a heterogeneous catalyst.

State a catalyst that can be used and why this is described as a *heterogeneous* catalyst. [2]

Nickel (or platinum).

The catalyst (solid) and the reactants and products are in different physical states.

(iv) One solvent that can be used for the hydrogenation described in (iii) above is hexane. The boiling temperatures of pentane and hexane are 35 °C and 69 °C respectively.

State the name of a method that can be used to separate these two compounds. [1]

Fractional distillation

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(v) The boiling temperatures of some alkanes are shown in the table.

Alkane	Boiling temperature / °C
2,2-dimethylpropane	9
2-methylbutane	28
pentane	35
2,2-dimethylbutane	50
2-methylpentane	60
hexane	69
heptane	98

State **two** factors that affect the boiling temperature of an alkane that can be deduced from the formulae of these alkanes. Suggest reasons for these variations in boiling temperatures. [4]

Chain length: as the chain length increases, so does the boiling temperature (pentane 35 °C, hexane 69 °C).

This rise is due to increased intermolecular (van der Waals) forces, so more energy is needed to separate the molecules.

Branching: as the isomers become more branched the boiling temperatures decrease.

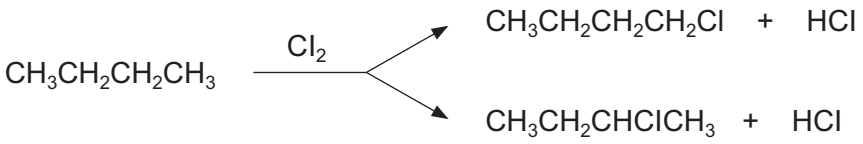
The branched isomers have less surface contact, so weaker intermolecular bonding.

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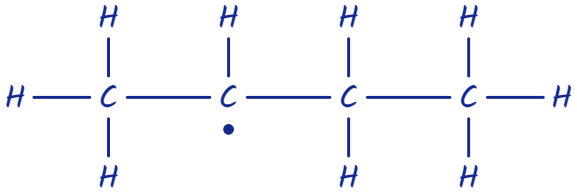
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(vi) A radical reaction occurs when alkanes are reacted with chlorine in the presence of ultraviolet light. For example in the chlorination of butane.



I. Give the **displayed** formula of the carbon-containing radical that leads to 2-chlorobutane. [1]



II. State the name of an alkane that can be made as a side product during the chlorination of butane. [1]

Octane (C_8H_{18})

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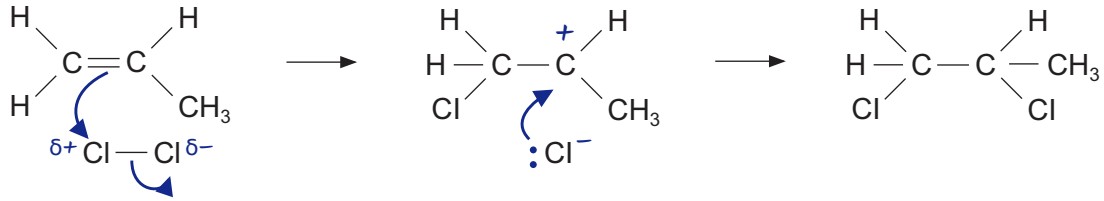
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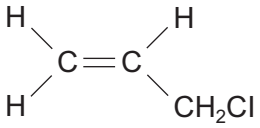
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12. *(a)* At room temperature propene reacts with chlorine by electrophilic addition.

Complete the mechanism for this reaction. [2]



(b) At 500 °C propene reacts with chlorine via a radical mechanism to give 3-chloropropene together with hydrogen chloride.



3-chloropropene

Describe a simple chemical test to distinguish between 1,2-dichloropropane [formed in part *(a)*] and 3-chloropropene. Give the reagent and the result with both compounds. [2]

Add bromine water (aqueous bromine) to each.

3-Chloropropene (alkene) decolourises it, orange to colourless;

1,2-dichloropropane (alkane) is unaffected and it stays orange.

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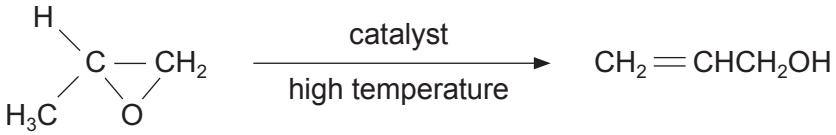
(c) (i) 3-Chloropropene can be converted to prop-2-en-1-ol by reaction with sodium hydroxide in a nucleophilic substitution reaction.

$$CH_2{=}CHCH_2Cl + NaOH \longrightarrow CH_2{=}CHCH_2OH + NaCl$$

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

^-OH (the hydroxide ion)

(ii) An alternative method of obtaining prop-2-en-1-ol is by the rearrangement of epoxypropane.



When choosing an appropriate method there are a number of factors to be considered.

Suggest **two** factors that should be considered if prop-2-en-1-ol is to be produced from epoxypropane rather than by the method described in part (i). [2]

1. Atom economy: the rearrangement has 100 % atom economy with no NaCl by-product, and the percentage yield.

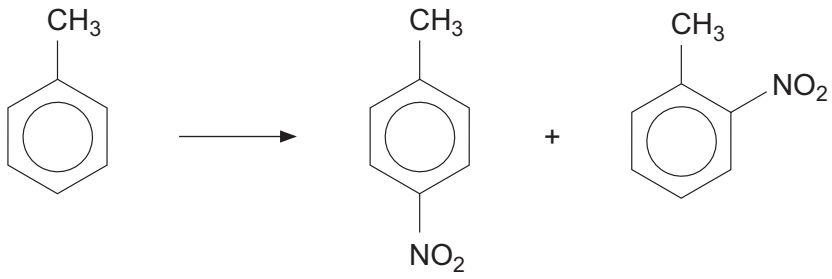
2. Cost and availability of the starting material and catalyst, including the cost of running the reaction at a high temperature.

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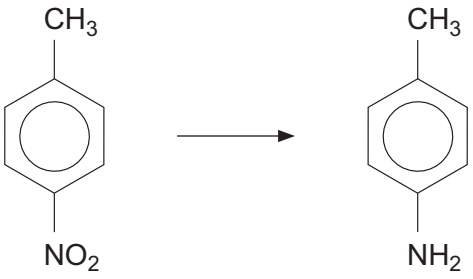
(d) Creosote is a pale yellow liquid that is used as a wood preservative. This material is largely a mixture of various phenols, including 4-methylphenol.

(i) In the laboratory 4-methylphenol can be made in several stages from methylbenzene.

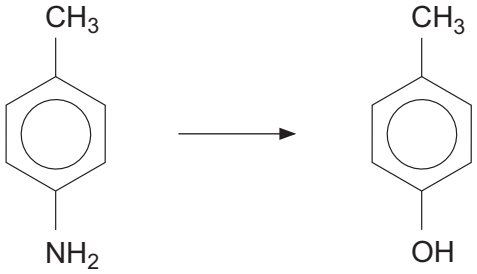
First stage The nitration of methylbenzene



Second stage The reduction of 4-nitromethylbenzene



Third stage Making 4-methylphenol from the amine 4-methylphenylamine

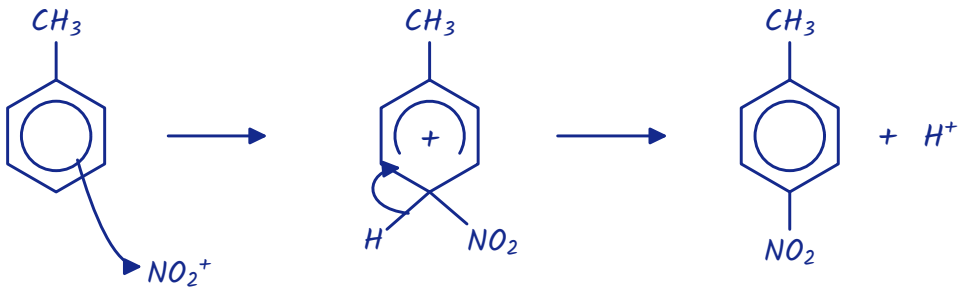


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I. Write the mechanism for the formation of 4-nitromethylbenzene, starting with methylbenzene and the nitronium ion. As part of your answer you should state the reagents used to generate the nitronium ion and name the type of reaction mechanism occurring. [4]



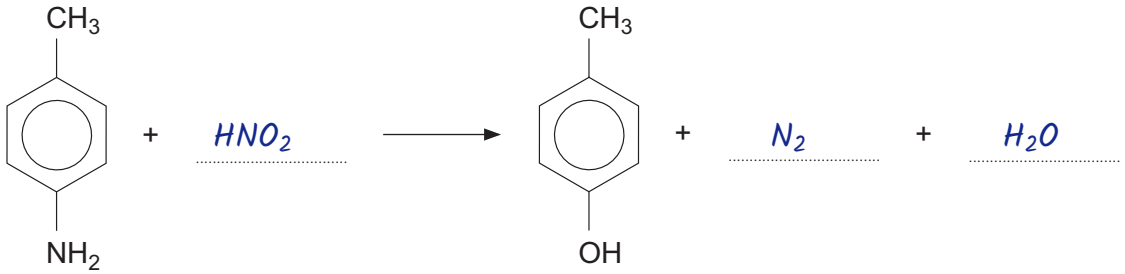
Reagents used *concentrated nitric acid and concentrated sulfuric acid*

Type of reaction mechanism *electrophilic substitution*

II. Suggest a suitable reducing agent used to produce 4-methylphenylamine from 4-nitromethylbenzene. [1]

Tin (or iron) and concentrated hydrochloric acid

III. Complete the equation below which shows the production of 4-methylphenol from 4-methylphenylamine. [2]



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(ii) pK_a is a term used to express the acidity of organic compounds. The lower the value, the greater the tendency for the compound to lose a hydrogen ion, making it more acidic.

The table shows the pK_a values for some compounds.

Compound	pK_a
ethanoic acid	4.8
4-nitrophenol	7.2
phenol	9.9
4-methylphenol	10.2

I. Ethanoic acid is more acidic than phenol. State a chemical test that you could use in the laboratory to show this difference in acidity. You are given aqueous solutions of each compound. [2]

Add sodium hydrogencarbonate ($NaHCO_3$) solution to each.

Ethanoic acid gives effervescence (CO_2 given off); phenol does not.

II. Suggest why 4-nitrophenol is much more acidic than phenol. [1]

The electron withdrawing NO_2 group weakens the O–H bond, and

the anion formed is more stable than the phenoxide ion.

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13. *(a)* Explain why amino acids are amphoteric compounds. [1]

They contain both an acidic (COOH) and a basic (NH_2) functional group.

(b) If an amino acid is treated with methanal, the resulting compound can be titrated against sodium hydroxide solution in a 1:1 ratio.

4.95 g of an amino acid was treated with methanal and the resulting solution made up to 250 cm^3. 25.0 cm^3 of this solution was then titrated with sodium hydroxide of concentration 0.105 mol dm^{-3}. The results are shown in the table below.

Titration	1	2	3	4	5
NaOH(aq) used / cm^3	38.70	35.90	36.00	32.00	36.10

(i) Suggest a practical reason why the reading for titration 1 was too high. [1]

The burette had been rinsed with water, which was not replaced entirely with sodium hydroxide solution.

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(ii) Use appropriate titration values to calculate the relative molecular mass of the amino acid. [5]

Concordant titres: 35.90, 36.00 and 36.10 cm^3

mean titre = (35.90 + 36.00 + 36.10) ÷ 3 = 36.00 cm^3

n(NaOH) = 36.00 × 0.105 ÷ 1000 = 0.00378 mol

1:1 ratio, so n(amino acid) in 25.0 cm^3 = 0.00378 mol

250 cm^3 contain 0.00378 × 10 = 0.0378 mol

M_r = 4.95 ÷ 0.0378 = 131

M_r = 131

(iii) Assuming that the amino acid in part (ii) is a straight chain aliphatic α-amino acid deduce its structure. [2]

$-CH(NH_2)COOH$ has 'M_r' = 74

'M_r' of chain = 131 − 74 = 57, so the chain is C_4H_9

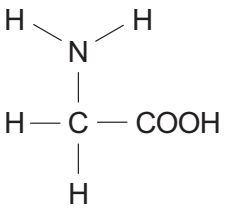
structure: $CH_3CH_2CH_2CH_2CH(NH_2)COOH$

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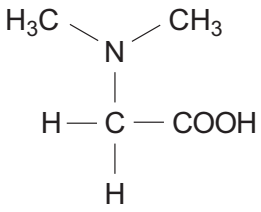
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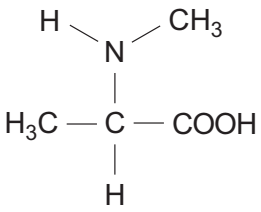
(c) The formulae of three amino acids are shown below.



compound **R**



compound **S**



compound **T**

(i) State which of the three compounds could be identified by its ability to rotate the plane of plane polarised light. Give a reason for your answer. [1]

Compound T, as it is the only one that contains a chiral centre (asymmetric carbon atom).

(ii) State how the infrared absorption spectrum of compounds **S** and **T** would differ from each other in their significant functional group absorption(s). [1]

Only compound T (which has an N–H bond) would show an N–H stretching absorption at 3300 to 3500 cm^{-1}.

(iii) State which of these amino acids would **not** be able to form two **different** dipeptides with either of the other two amino acids. Explain your answer. [1]

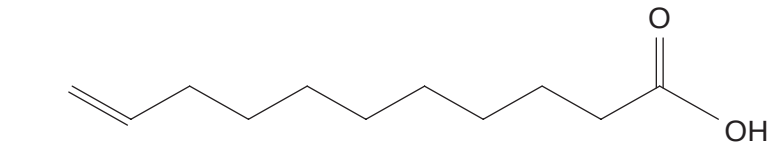
Compound S: it could only form one dipeptide, via its COOH group, as its N does not have an N–H bond.

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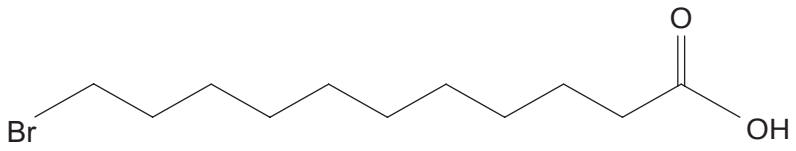
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(d) Nylon-11 is a bio-sourced polyamide which is made from castor oil. Undec-10-enoic acid is produced as an intermediate compound. This acid is reacted, under suitable conditions, to give 11-bromoundecanoic acid, which is then treated with ammonia to produce 11-aminoundecanoic acid. Polymerisation of this product gives nylon-11.



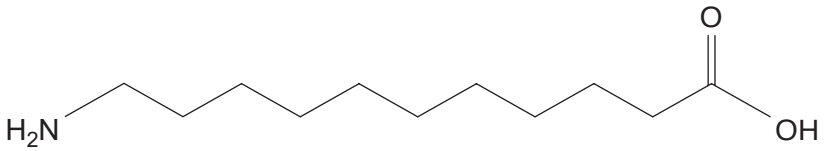
undec-10-enoic acid





11-bromoundecanoic acid





11-aminoundecanoic acid

(i) The addition of hydrogen bromide to undec-10-enoic acid would give 10-bromoundecanoic acid as the major product. Explain why this is the case. [1]

The reaction proceeds via a secondary carbocation (on C10), which is more stable than the primary carbocation and so has a lower activation energy (Markovnikov's rule).

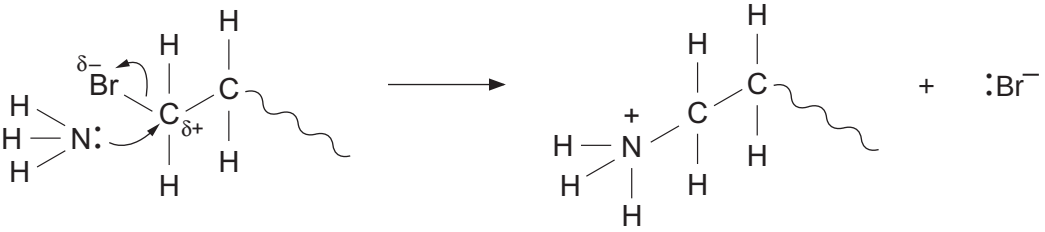
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(ii) The bromo-compound reacts with ammonia to produce 11-aminoundecanoic acid.

One step in the mechanism for this reaction is shown below.



I. Explain how partial charges (δ+ and δ–) arise on the carbon and bromine atoms. [1]

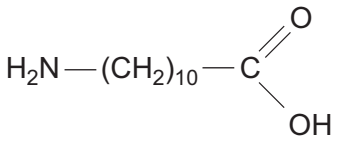
Bromine is more electronegative than carbon (greater electron attracting power), so Br is δ– and C is δ+.

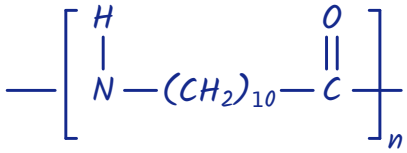
II. State the role of ammonia in this reaction. [1]

It acts as a nucleophile (lone pair donor).

(iii) Draw the structure of nylon-11, indicating the repeating unit present.

The formula of 11-aminoundecanoic acid is shown below. [1]





repeating unit (in brackets)

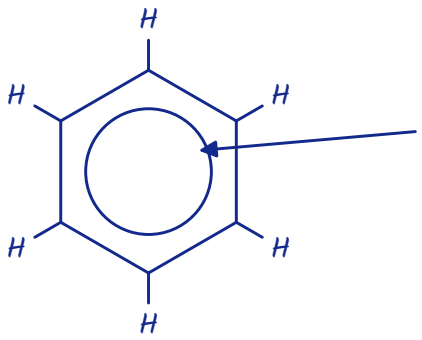
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14. *(a)* (i) Describe the structure and bonding in benzene. Explain why benzene is resistant to addition reactions and why its usual mode of reaction is by substitution.

You may include a diagram as part of your answer. [4]



delocalised π electrons above and below the planar ring; all C–C bonds the same length, bond angles 120°

Benzene, C_6H_6, is a planar six-membered ring. Each C forms three σ bonds and its fourth electron is in a p orbital; these overlap to form a delocalised π cloud.

This delocalisation gives extra stability, which would be lost if addition occurred.

Substitution keeps the delocalised system, so it is the usual reaction.

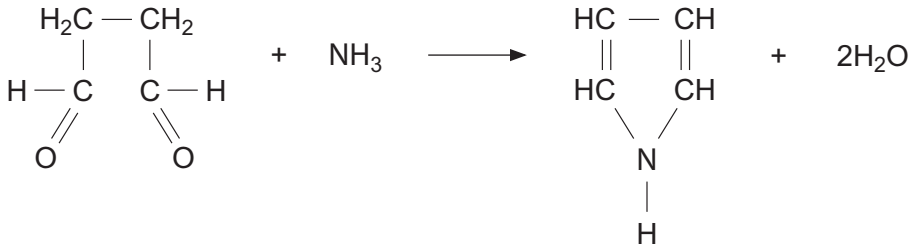
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(ii) Benzene is an example of an aromatic compound. There are a number of other aromatic systems. One of these is pyrrole.

I. Pyrrole can be made by reacting butan-1,4-dial with ammonia.



Calculate the atom economy of this reaction. [2]

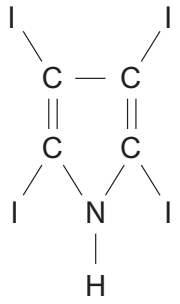
M_r: butan-1,4-dial $C_4H_6O_2$ = 86.0, NH_3 = 17.0, pyrrole C_4H_5N = 67.0

atom economy = 67.0 ÷ (86.0 + 17.0) × 100

Atom economy = 65.0 %

II. Pyrrole reacts in a similar way to benzene, although it is more reactive.

For example, pyrrole reacts readily with iodine to produce 2,3,4,5-tetraiodopyrrole.



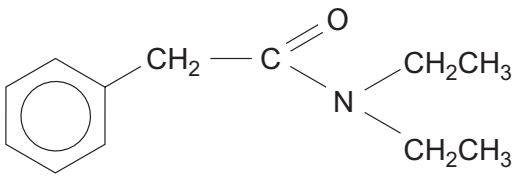
Suggest the balanced equation for the reaction between iodine and pyrrole, leading to 2,3,4,5-tetraiodopyrrole. [1]

$C_4H_4NH + 4I_2 \rightarrow C_4I_4NH + 4HI$

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(b) Diseases caused by sucking insects are a major problem in hot countries. Extensive research has been carried out to find compounds that are deterrents against these insects. One of the these compounds is DEPA.



DEPA

(i) In the first stage of a synthesis of DEPA, methylbenzene [M_r 92.1] reacts with chlorine until the increase in mass indicates that (chloromethyl)benzene, $C_6H_5CH_2Cl$ [M_r 126.6] has been produced.

In an experiment 0.430 mol of methylbenzene was used. Calculate the increase in mass that will indicate that the conversion to $C_6H_5CH_2Cl$ is complete. [2]

mass of methylbenzene = 92.1 × 0.430 = 39.6 g

mass of $C_6H_5CH_2Cl$ = 126.6 × 0.430 = 54.4 g

increase = 54.4 − 39.6 = 14.8 g

Increase in mass = 14.8 ..... g

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(ii) Suggest a three stage synthesis of phenylethanoic acid ($C_6H_5CH_2COOH$) starting from methylbenzene. In the first stage, methylbenzene reacts with chlorine in a similar way to the reaction of chlorine with methane.

For each stage you should state the reactants and the products as well as any important conditions, relevant equations and the type of reaction or mechanism occurring. [6 QER]

Stage 1: methylbenzene reacts with chlorine in the presence of UV light by radical substitution (homolytic fission of Cl_2), giving (chloromethyl)benzene: $C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$

Stage 2: (chloromethyl)benzene is heated under reflux with potassium cyanide in ethanol. The CN^- ion acts as the nucleophile in a nucleophilic substitution, adding one carbon atom: $C_6H_5CH_2Cl + KCN \rightarrow C_6H_5CH_2CN + KCl$

Stage 3: hydrolysis of the nitrile by heating under reflux with aqueous acid (e.g. dilute HCl), via the amide: $C_6H_5CH_2CN \rightarrow C_6H_5CH_2CONH_2 \rightarrow C_6H_5CH_2COOH$

Overall: $C_6H_5CH_2CN + 2H_2O + H^+ \rightarrow C_6H_5CH_2COOH + NH_4^+$

(iii) The overall yield of phenylethanoic acid, starting from methylbenzene, was 65 %.

Calculate the mass of phenylethanoic acid [M_r 136] formed from 0.430 mol of methylbenzene. [1]

mass = 0.430 × 0.65 × 136

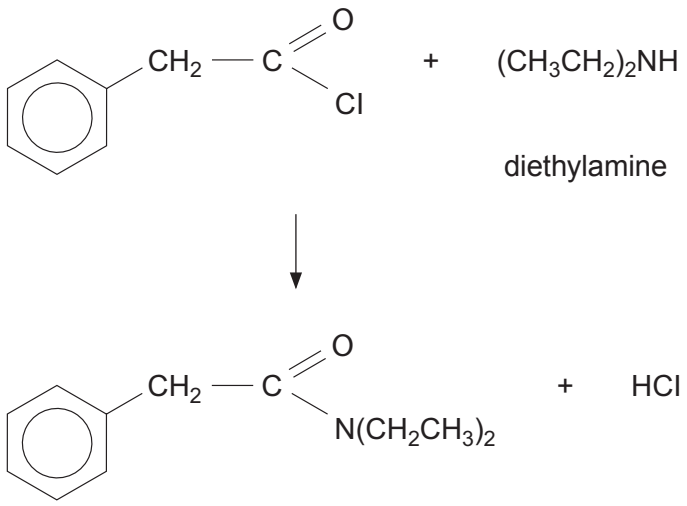
Mass = 38.0 g

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(iv) The final stage to make DEPA is shown in the equation below.



DEPA

A teacher asked some students for suggestions as to how this reaction should be carried out.

I. One student suggested that the reaction could be carried out using water as the solvent.

Suggest why this method might give a very poor yield of DEPA. [1]

The acid chloride may react preferentially with the water present rather than with the amine.

II. Another suggestion was that an excess of diethylamine should be used.

Explain why this method should be used. [1]

So that the hydrogen chloride produced is neutralised by the excess diethylamine.

III. A further suggestion was that DEPA should be purified by distillation under reduced pressure as DEPA is a liquid with a high boiling temperature.

Explain why this process of separation should be used. [1]

Reduced pressure lowers the boiling temperature, avoiding decomposition at the higher temperature of ordinary distillation.

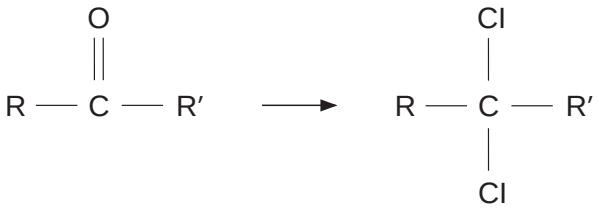
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15. *(a)* Ketone **W** reacted with phosphorus(V) chloride to give the corresponding dichloro compound.



ketone **W**

(i) Describe how to show the presence of chlorine in this compound. [4]

Warm the compound with aqueous sodium hydroxide (with ethanol as a co-solvent).

Acidify the mixture with dilute nitric acid.

Add silver nitrate solution.

A white precipitate (AgCl) is seen, which dissolves in aqueous ammonia.

(ii) 6.35 g of the dichloro compound formed from ketone **W** contained 50.3 % of chlorine by mass, the remainder being carbon and hydrogen.

Calculate the relative molecular mass of the dichloro compound. [2]

mass of chlorine = 6.35 × 0.503 = 3.19 g

moles of Cl = 3.19 ÷ 35.5 = 0.0900 mol

2 Cl per molecule: moles of compound = 0.0450 mol

M_r = 6.35 ÷ 0.0450 = 141

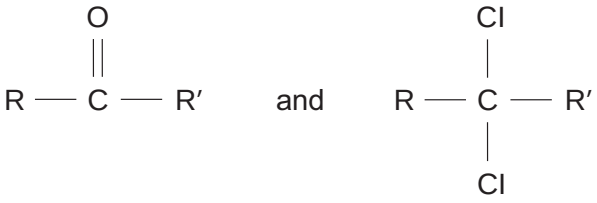
M_r = 141

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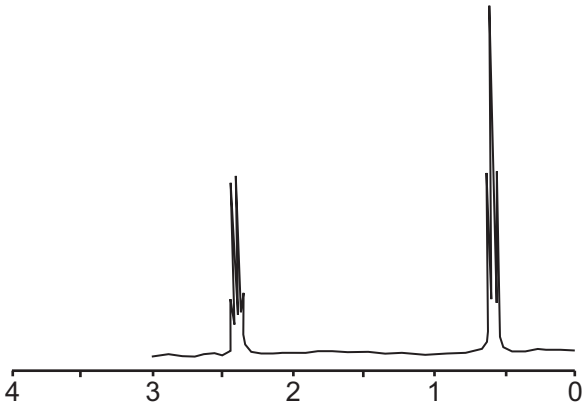
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(iii) Explain why both the molecules shown below have the same splitting pattern in their ^{1}H NMR high resolution spectra. [1]



There are no protons bonded to the central carbon atom in either compound, so the splitting pattern of the R and R' protons is not affected by the chlorination.

(iv) The ^{1}H NMR spectrum of ketone **W** is shown below.



Assuming that the alkyl groups R and R′ are the same, use the information from the NMR spectrum to deduce the structure of ketone **W**. [3]

Data Booklet: the peak at about 2.4 ppm is H on C next to C=O (2.0 to 3.0 ppm); the peak below 1 ppm is alkyl H (0.1 to 2.0 ppm).

The 2.4 ppm peak is a quartet (CH_2 next to CH_3) and the other is a triplet (CH_3 next to CH_2), so R and R' are ethyl groups.

Ketone W is $CH_3CH_2C(O)CH_2CH_3$ (pentan-3-one).

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(b) The relative molecular mass of a volatile compound **L** can be found by weighing a sample and measuring the volume of its vapour at a known temperature and pressure.

(i) In an experiment the following results were obtained.

Mass of liquid **L** = 0.222 g
Volume of vapour produced = 111 cm^3
Temperature = 423 K
Pressure = 9.50×10^4 Pa

Use this data to calculate the relative molecular mass of compound **L**. [2]

$pV = nRT$

$9.50 \times 10^4 \times 111 \times 10^{-6} = n \times 8.31 \times 423$

$n = 0.00300$ mol

$M_r = 0.222 \div 0.00300 = 74$

M_r = 74

(ii) Tests on liquid **L** showed that

- it did not liberate carbon dioxide with sodium hydrogencarbonate solution.
- it contained 2 oxygen atoms in each molecule
- when it was heated with aqueous sodium hydroxide it did **not** produce ethanol as one of the products

Discuss these results and then suggest a structure for liquid **L**. [4]

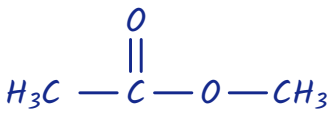
No CO_2 with $NaHCO_3$, so it is not a carboxylic acid (no COOH group).

Two oxygen atoms per molecule (M_r 74, $C_3H_6O_2$) suggests an ester:

$HCOOCH_2CH_3$ or CH_3COOCH_3.

Not ethyl methanoate, since this would give ethanol on hydrolysis, so L is

methyl ethanoate:



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