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9791/03

May/June 2016

2 hours 15 minutes

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

DO **NOT** WRITE IN ANY BARCODES.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
Total	

The syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

This document consists of **20** printed pages and **4** blank pages.

- 1 (a) The kinetic theory of gases makes assumptions about the behaviour of an ideal gas. Boyle and Charles were amongst the first scientists to make detailed experimental measurements of the behaviour of gases.

(i) State **three** assumptions of the kinetic theory of gases.

.....

.....

.....

.....[3]

(ii) State Boyle's law.

.....

.....[1]

(iii) State Charles's law.

.....

.....[1]

(iv) State the conditions of temperature and pressure under which you might expect the behaviour of a real gas to be **least** like that of an ideal gas. Explain your answers.

temperature

explanation

.....

.....

pressure

explanation

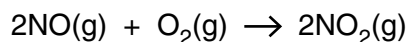
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[3]

- (v) Suggest the order in which you would expect the following real gases to deviate from the behaviour of an ideal gas. List the gas with the **most** ideal behaviour first. Explain your order.

(c) The kinetics of the gas phase reaction



were studied at a temperature of 80K in a 1.00dm^3 flask and the initial reaction rates were measured for varying initial amounts of the reactants.

experiment	initial amount/mol		initial rate of NO_2 formation / $\text{mol dm}^{-3}\text{s}^{-1}$
	NO	O_2	
1	1.25×10^{-3}	1.25×10^{-3}	1.15×10^{-14}
2	2.50×10^{-3}	1.25×10^{-3}	4.61×10^{-14}
3	1.25×10^{-3}	2.50×10^{-3}	2.30×10^{-14}

- (i) Explain how the data can be used to determine the orders of reaction with respect to NO and O_2 and hence derive the rate equation for this reaction.

.....

.....

.....

.....

.....

rate equation [3]

- (ii) Use the data from experiment 1 to calculate the value of the rate constant, k , at 80 K. Give the units of k .

$k = \dots\dots\dots$ units [2]

- (iii) Use the data from experiment 1 and the ideal gas equation to calculate the initial pressure in the flask.

pressure = Pa [2]

[Total: 25]

- 2 Some chemical reactions proceed to a dynamic equilibrium containing appreciable amounts of both reactants and products.

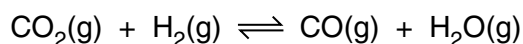
(a) (i) Give one characteristic of a dynamic equilibrium.

.....
.....[1]

(ii) State Le Chatelier's principle.

.....
.....
.....[1]

- (b) Carbon dioxide and hydrogen react together to form an equilibrium mixture.



- (i) Give the expression for K_c for this equilibrium.

$$K_c =$$

[1]

- (ii) The values of K_c at two different temperatures are shown in the table.

temperature/°C	K_c
700	0.63
1000	1.66

State and explain what the values of K_c indicate about the enthalpy change for this reaction.

.....
[1]

- (iii) State and explain the effect of increasing pressure on the position of this equilibrium.

.....

[2]

- (iv) 0.0100 mol of CO_2 and 0.0200 mol of H_2 were mixed and allowed to reach equilibrium at a temperature T . The final mixture contained 6.93×10^{-3} mol of H_2O .

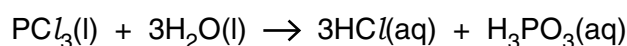
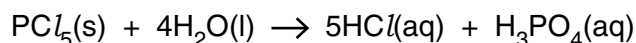
Calculate the value of K_c at this temperature.

$$K_c = \dots\dots\dots [3]$$

- (c) A 0.100 mol sample of PCl_5 vapour was heated in a flask until the following equilibrium was established.



The resulting mixture of gases was cooled rapidly to form solid PCl_5 and liquid PCl_3 . The chlorine gas was pumped away and water was added to the mixture of chlorides to hydrolyse them. The following reactions occurred.



The solution resulting from hydrolysis of the chlorides was made up to 1.00 dm^3 and labelled solution **A**.

A 10.0 cm^3 sample of solution **A** required 31.40 cm^3 of 0.200 mol dm^{-3} sodium hydroxide solution, $\text{NaOH}(\text{aq})$, for neutralisation.

Assume that in the neutralisation 1 mole of H_3PO_4 reacts with 2 moles of NaOH .

Assume that in the neutralisation 1 mole of H_3PO_3 reacts with 2 moles of NaOH .

- (i) Calculate the total amount, in mol, of $\text{OH}^-(\text{aq})$ needed for neutralisation of the 1.00 dm^3 of solution **A**.

amount of $\text{OH}^-(\text{aq}) = \dots\dots\dots\text{ mol}$ [2]

- (ii) Calculate the amount, in mol, of PCl_5 in the equilibrium mixture.

amount of $\text{PCl}_5 = \dots\dots\dots\text{ mol}$ [3]

[Total: 14]

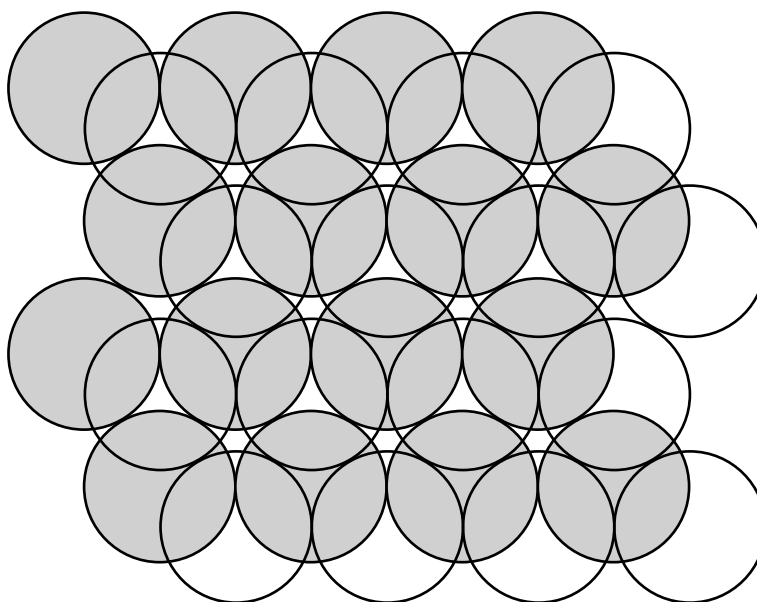
- 3 (a) Most metals have a close-packed structure based on one of two possible arrangements of atoms, CCP or HCP.

(i) What is the co-ordination number of an atom in a close-packed structure?

..... [1]

(ii) Both of the close-packed structures can be represented as a layer structure.

Two layers are shown with the shaded circles representing atoms in the first layer and the unshaded circles representing atoms in the second layer.



Add labels to the diagram to show clearly the positions of

- the centres of **two** atoms in the third layer of a CCP structure, labelled *****,
- a tetrahedral hole, labelled **T**,
- an octahedral hole, labelled **O**.

[3]

(iii) In terms of the type of holes occupied and the ratio of holes to ions, describe the lattice structure of calcium fluoride.

.....

 [2]

(b) Tin forms two chlorides, SnCl_2 and SnCl_4 .

(i) A sample of a mixture of these chlorides was found to contain 50.0% by mass of tin.

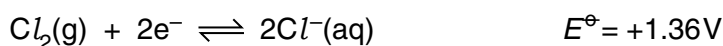
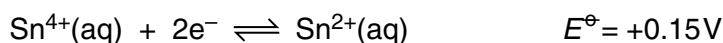
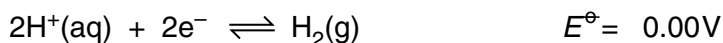
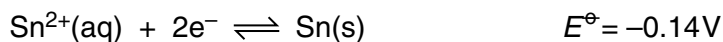
Calculate the percentage by mass of SnCl_2 in the sample.
You must show your working.

% = [3]

(ii) Heating tin with hydrochloric acid produces hydrogen gas. Careful evaporation of the water and dehydration with ethanoic anhydride produces white solid SnCl_2 .

Passing chlorine gas over heated tin produces colourless liquid SnCl_4 as the only product.

Discuss whether the following standard electrode potentials support the production of SnCl_2 with hydrochloric acid and the production of SnCl_4 with chlorine.



.....

[3]

(c) Each element in Group 14 can form a monoxide.

- (i) Draw a dot-cross diagram, showing outer-shell electrons only, to show the bonding in carbon monoxide, CO.

[1]

- (ii) State and explain the trend in the type of **bonding** in the monoxides down Group 14.

.....

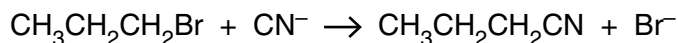
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.....

.....[2]

[Total: 15]

- 4 (a) Heating 1-bromopropane under reflux with potassium cyanide in ethanol produces butanenitrile.



- (i) This reaction proceeds via a transition state.

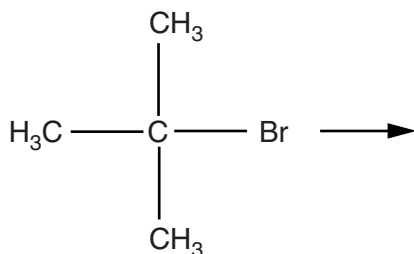
Draw the first step of the mechanism leading to the formation of the transition state. Include all relevant lone pairs of electrons, dipoles and curly arrows.

Draw the three-dimensional structure of the transition state and give the bond angles. Represent the ethyl group as C_2H_5 .

[5]

- (ii) Complete the first step of the mechanism for the reaction of 2-methyl-2-bromopropane with cyanide ions. Include all relevant lone pairs of electrons, dipoles and curly arrows.

Explain why the mechanism is different from that of the reaction involving 1-bromopropane with cyanide ions.



.....

.....

.....

[3]

- (b) Butanenitrile, $\text{C}_3\text{H}_7\text{CN}$, reacts with aqueous acid to form an intermediate compound, **S**, which then reacts further to form compound **T**.

(i) Write an equation to show the formation of **S** from $\text{C}_3\text{H}_7\text{CN}$.

.....[1]

(ii) Write an equation to show the formation of **T** from **S**.

.....[1]

(iii) Identify the type of reaction involved in the overall conversion of $\text{C}_3\text{H}_7\text{CN}$ to **T**.

Justify your answer with reference to functional group level.

.....
.....
.....[2]

- (c) Butanenitrile, $\text{C}_3\text{H}_7\text{CN}$, reacts with lithium tetrahydridoaluminate, LiAlH_4 , to form compound **U**.

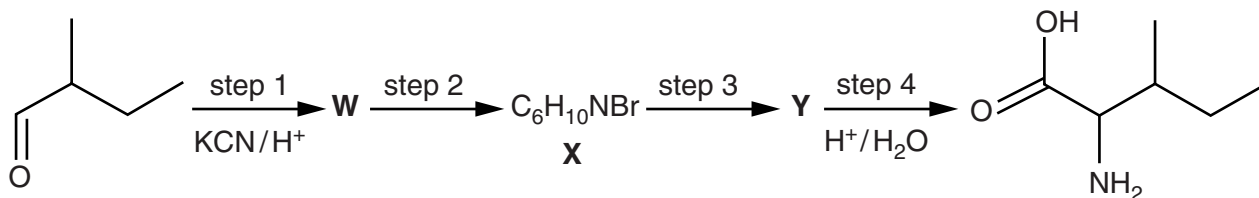
Identify **U** and the type of reaction involved in the conversion of $\text{C}_3\text{H}_7\text{CN}$ to **U**.

Justify your answer with reference to functional group level.

.....
.....
.....[3]

- (d) A nitrile group can react with carbonyl compounds. This reaction can form the basis for the synthesis of amino acids.

The amino acid isoleucine can be prepared by a four-step sequence starting from 2-methylbutanal and cyanide ions.



- (i) Give the full name of the reaction mechanism involved in step 1.

.....[1]

- (ii) Draw the **skeletal** formula for **W**.

[1]

- (iii) Suggest the full name of the reaction mechanism involved in step 2.

.....[1]

- (iv) State the reagent needed for step 2.

.....[1]

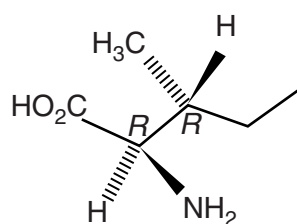
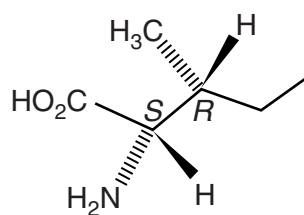
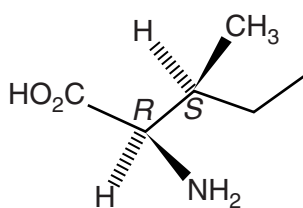
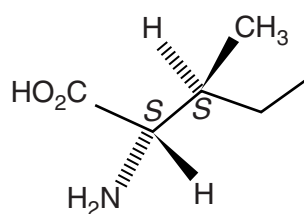
- (v) State the reagents and conditions needed for step 3.

.....
[2]

- (vi) Give the **structural** formula of **Y**.

.....[1]

(vii) There are four stereoisomers of isoleucine.

**A****B****C****D**

Identify by letter all those **pairs** of isomers that are either enantiomers or diastereoisomers of each other.

enantiomers

diastereoisomers

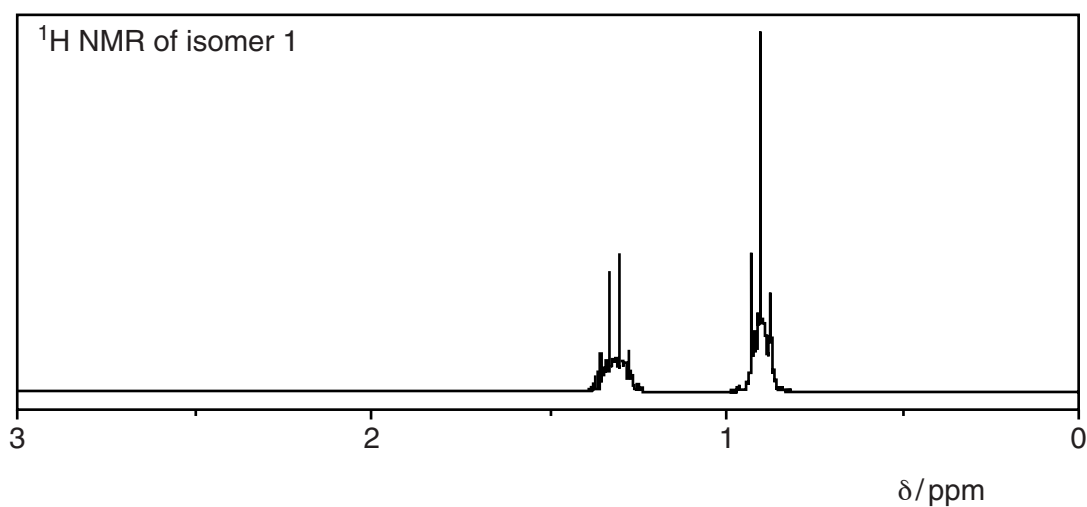
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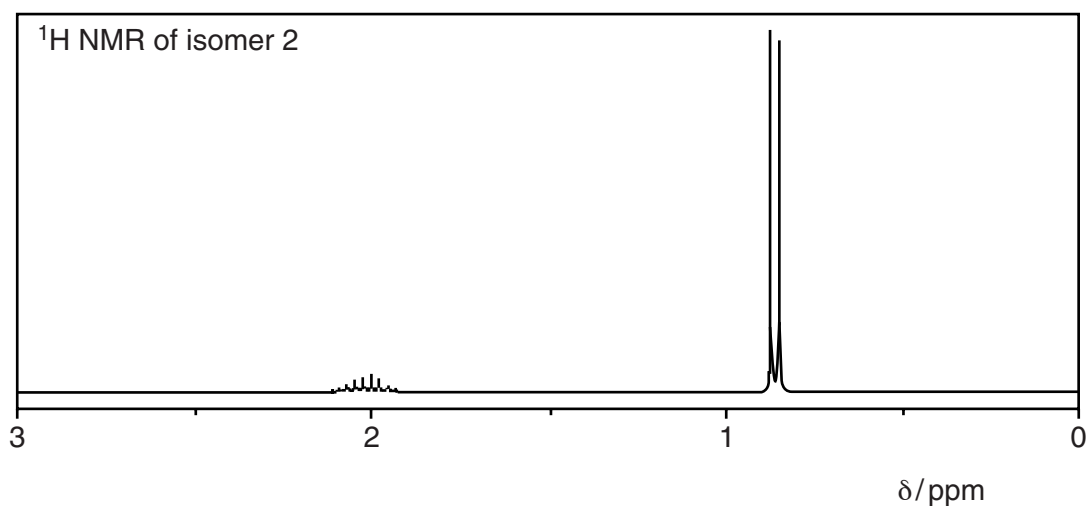
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- 5 (a) Two hydrocarbons have a molecular ion peak at m/z of 58.

The ^1H NMR spectrum of isomer 1 may be analysed by seeing that it consists predominantly of a triplet and a quartet.



The ^1H NMR spectrum of isomer 2 consists of a doublet and a decet (10 peaks).



- (i) What is the molecular formula of both isomers?

.....[1]

- (ii) Give the structural formula of each isomer and explain the splitting patterns of the signals in each ^1H NMR spectrum.

isomer 1

.....

.....

.....

isomer 2

.....

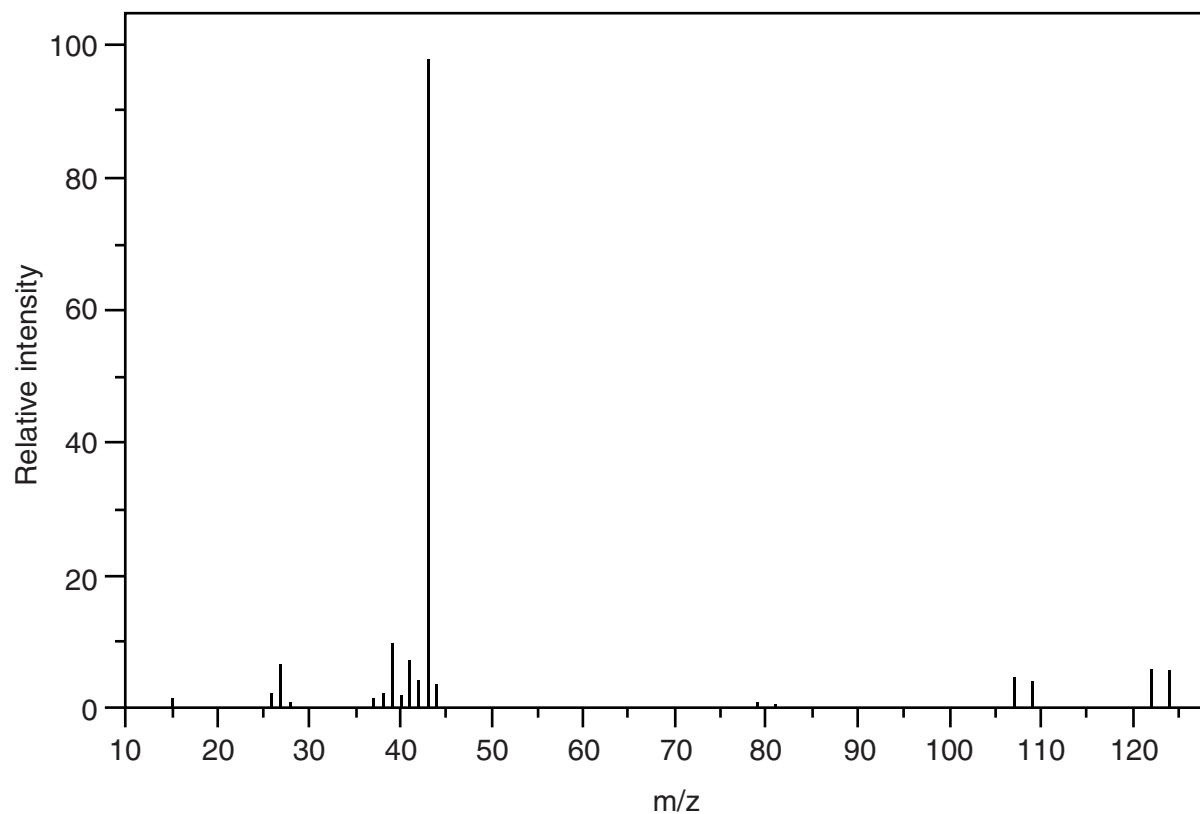
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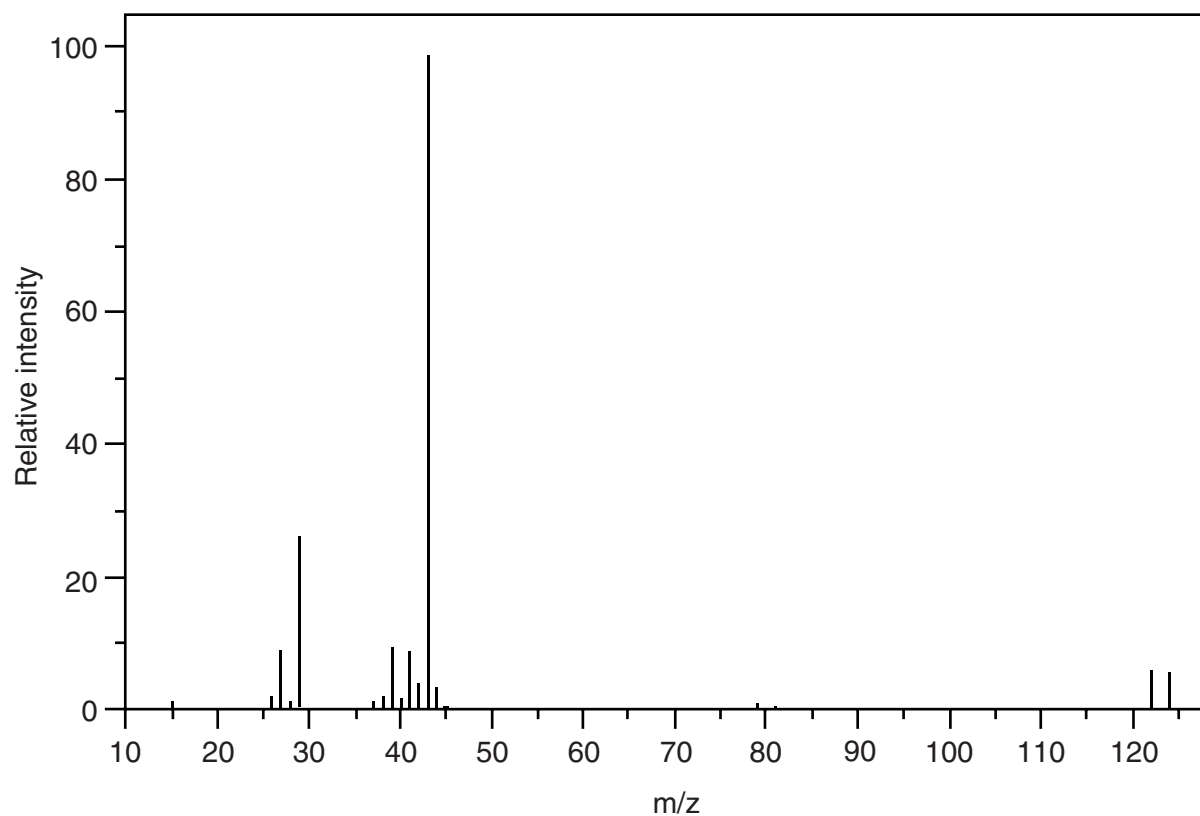
[3]

(b) Two isomeric halogenoalkanes have the mass spectra shown.

Isomer 3 has key peaks at m/z values of 124, 122, 109, 107 and 43.



Isomer 4 has key peaks at m/z values of 124, 122, 43 and 29.



- (i) Explain the significance of the peaks at m/z 124 and 122 in both spectra and their equal relative intensities.

.....
.....
.....[2]

- (ii) What is the molecular formula of the two isomers?

.....[1]

- (iii) Give the structural formulae of isomers 3 and 4 and explain your choice by referring to the key peaks which are unique to each spectrum.

isomer 3

isomer 4

explanation
.....
.....
.....[3]

- (iv) Starting from the molecular ion, write an equation to explain the formation of the fragment responsible for the peak at m/z 43.

.....[2]

- (c) Three unbranched carbonyl compounds have the molecular formula $C_5H_{10}O$.

Each is converted to an alcohol by reaction with anhydrous ethyl magnesium bromide, followed by acid hydrolysis.

Isomer 5 forms a chiral secondary alcohol.

Isomer 6 forms a chiral tertiary alcohol.

Isomer 7 forms a tertiary alcohol that is not chiral.

- (i) Give the structural formula of each isomer and the structural formula of the alcohol formed from it.

isomer 5

alcohol formed from isomer 5

isomer 6

alcohol formed from isomer 6

isomer 7

alcohol formed from isomer 7

[3]

- (ii) Write an equation for the overall reaction of methanal with ethyl magnesium bromide, followed by hydrolysis.

.....[2]

(d) Four aromatic compounds have the molecular formula C_7H_8O .

All four isomers react with sodium to form hydrogen gas.

Isomers 8, 9 and 10 react with sodium hydroxide to form salts, but isomer 11 does not.

The ^{13}C NMR spectrum of isomer 8 and isomer 9 both show seven separate signals.

The ^{13}C NMR spectrum of isomer 10 only shows five signals.

(i) Suggest a possible structure for each isomer.

isomer 8

isomer 9

isomer 10

isomer 11

[3]

(ii) Give approximate chemical shift values for the peaks you would expect to see in the ^{13}C NMR spectrum of isomer 11.

.....
.....[1]

[Total: 21]

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