

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 1

CANDIDATE
NAME

Answers

CLASS

TUTOR'S
NAME

CHEMISTRY

8872/02

Paper 2

14 September 2016

2 hours

Candidates answer Section A on the Question Paper

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A

Answer **all** questions on the question paper.

Section B

Answer **two** questions on the writing paper provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use

A1 / 8

A2 / 6

A3 / 26

B1 / 20

B2 / 20

B3 / 20

Total / 80

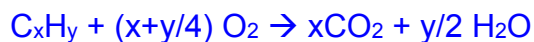
Section A

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

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- 1(a)(i) A gaseous aromatic hydrocarbon, **X**, was subjected to combustion analysis. **X** on complete combustion gave 0.814 g of carbon dioxide and 0.208 g of water. What is the empirical formula of **X**?

[2]



$$n(C) = n(CO_2) = 0.814/44 = 0.0185 \text{ mol}$$

$$n(H) = 2 \times n(H_2O) = 2 \times 0.208/18 = 0.02311 \text{ mol} \text{ [1]}$$

	C	H
Amount / mol	0.0185	0.02311
Mole ratio	$0.0185/0.0185 = 1$	$0.02311/0.0185 = 1.25$
Simplest ratio	4	5

Empirical formula of **X** = C_4H_5 [1]

- (ii) A 0.245 g sample of **X** has a volume of 51.8 cm³ at standard temperature and pressure. Determine the molecular formula of **X**.

[2]

$$n(X) = 51.8/1000 \div 22.4 = 0.002313 \text{ mol}$$

$$M_r(X) = 0.245 \div 0.002313 = 106 \text{ [1]}$$

Let the molecular formula of **X** be $(C_4H_5)_n$

$$48n + 5n = 106$$

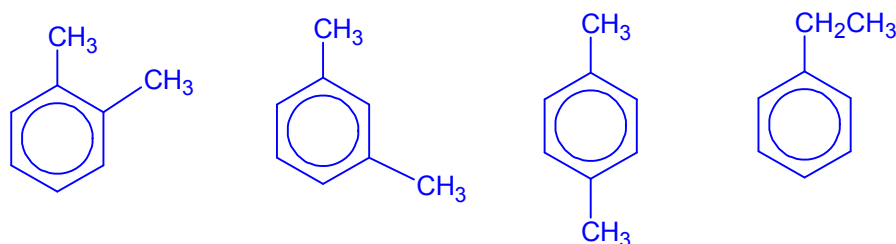
$$53n = 106$$

$$n = 2$$

Therefore the molecular formula of **X** = C_8H_{10} . [1]

- (iii) Draw all the structural isomers of the aromatic hydrocarbon, **X**.

[2]



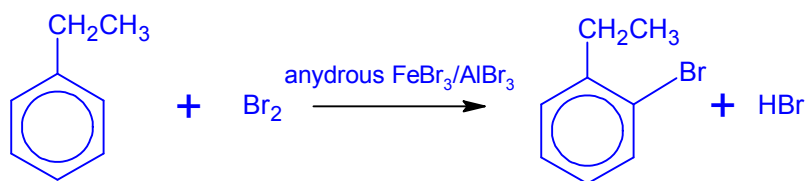
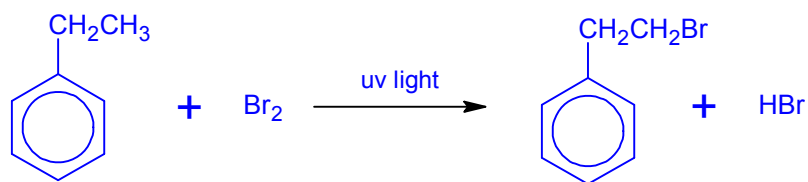
4 structures – 2 m

3, 2 structures – 1 m

- (iv) **X** can undergo two different halogenation reactions with bromine. Write an equation and state the conditions necessary for each of these reactions to occur.

[Total: 8]

Choosing any isomer of **X**,



either ortho or para product to be drawn

- 1st balanced equation correct
- 2nd balanced equation correct
- 1st reagent and condition
- 2nd reagent and condition

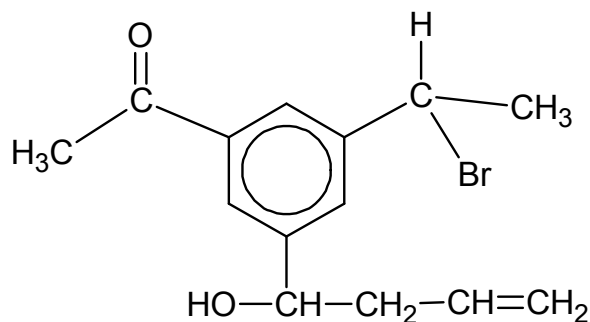
1 • = 0 mark

2 • = 1 mark

3 • = 1 mark

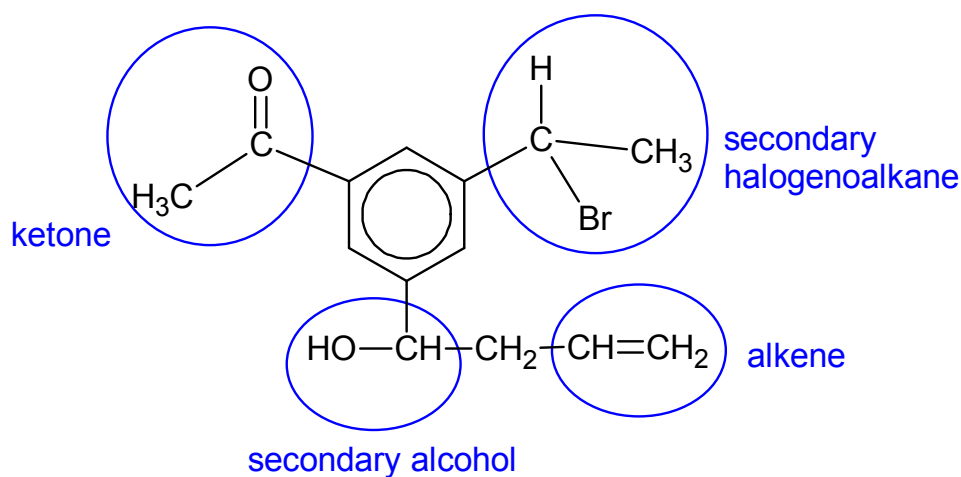
4 • = 2 marks

- 2 Compound **Z** has the following structure.



- (a) On the structure above, circle and name four different functional groups present in **Z** that are neither benzene rings nor alkyl groups.

[2]



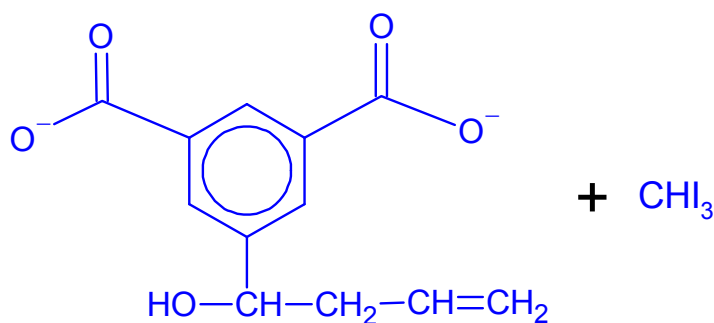
4 functional groups: [2]

2 or 3 functional groups: [1]

- (b) Draw the structural formulae of the organic products formed when **Z** reacts with

- (i) warm alkaline aqueous iodine

[3]

[1] for CHI_3

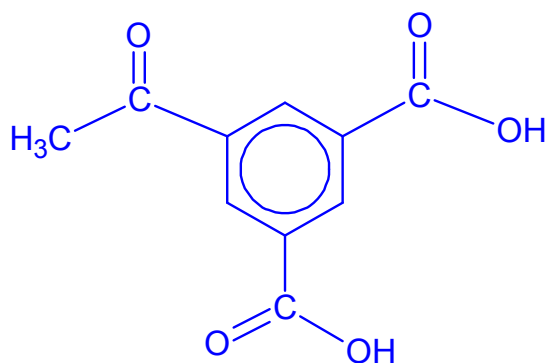
[1] for oxidation of methyl carbonyl

[1] for substitution of RX followed by oxidation of methyl alcohol

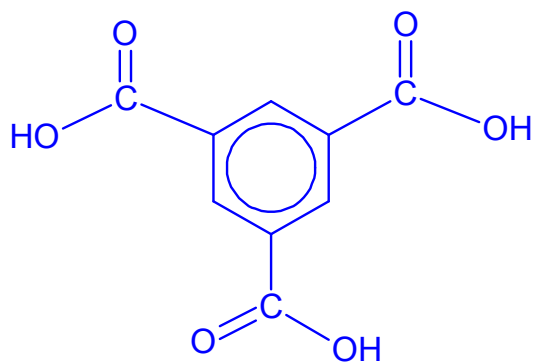
(ii) hot, acidified manganate(VII) ions

[1]

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OR



[1]

[Total: 6]

3 This question is about phosphorus and its chlorides.

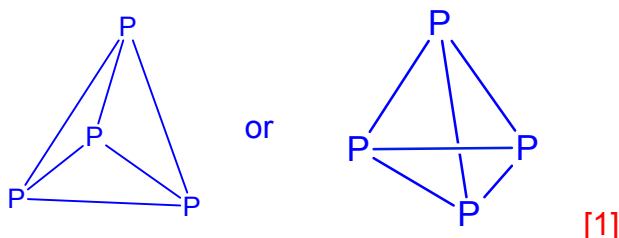
- (a) Allotropes are two (or more) forms of the same element, in which the atoms or molecules are arranged in different ways.

Elemental phosphorus can exist in several allotropic forms, the most common are white phosphorus and red phosphorus.

When heated to 400 °C in the absence of air, white phosphorus changes into the red form of the element.

- (i) White phosphorus exists as molecules made up of four atoms in a tetrahedral structure. Draw the structure of white phosphorus.

[1]



- (ii) The melting point of white phosphorus and red phosphorus are 44 °C and 500 °C respectively. Explain the difference in their melting points.

[2]

The white allotrope has a simple molecular structure with weaker van der Waals forces of attraction between P₄ molecules. [1] SBP

The red allotrope has a giant molecular structure with strong covalent bonds between P atoms. [1] SBP

More energy is required to break the stronger covalent bonds hence red phosphorus has a higher melting point.

- (b) Describe how separate samples of phosphorus(III) chloride, PCl₃, and phosphorus(V) chloride, PCl₅ can be made in the laboratory.

[2]

PCl₃ can be made by reacting phosphorous with limited chlorine.

PCl₅ can be made by reacting phosphorous with excess chlorine.

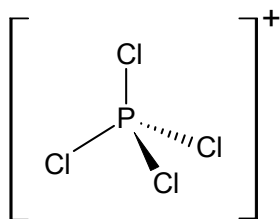
[1] Cl₂ reagent

[1] limited vs excess

- (c) Phosphorus(V) chloride is a white solid which sublimes at 160 °C. It dissolves in some polar solvents without reaction and such solutions conduct electricity. This is due to the presence of the two ions, [PCl₄]⁺ and [PCl₆]⁻.

Draw the structure and suggest the shape of **each** of these ions.

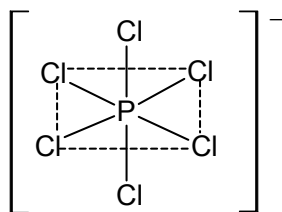
[3]



[1] 3D shape

tetrahedral

[1] both correct



[1] 3D shape

octahedral

- (d) When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.



Write an expression for K_c for this equilibrium, stating its units.

[2]

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \quad \text{units: mol dm}^{-3} \quad [1]$$

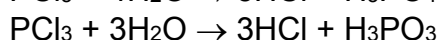
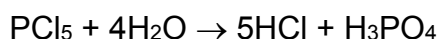
[1]

- (e) In an experiment, 1.00 mol of PCl_5 vapour was heated in a closed 5.00 dm³ flask at 500 K until equilibrium has been established.

The gases in the flask were then *rapidly cooled*, causing the formation of crystals of PCl_5 and liquid PCl_3 . The chlorine gas present was pumped away and collected.

The amount of chlorine collected was x mol.

An excess of water was then *very carefully added* to the two remaining compounds, under suitable conditions, causing the following reactions to occur. The addition of water may cause the mixture to boil.



You may assume that both H_3PO_4 and H_3PO_3 behave as *dibasic (diprotic) strong acids*.

- (i) Explain why the gases in the flask need to be *rapidly cooled*.

[1]

To prevent further reaction so that the equilibrium concentrations obtained would be accurate. [1]

- (ii) State and explain the reactions of PCl_5 and PCl_3 in water.

[2]

PCl_5 and PCl_3 hydrolyse in water. [1] type of reaction

When PCl_5 and PCl_3 dissolves in water, the δ^+ P atom attracts the δ^- O atom from water molecule. The O–H bond is broken, releasing a H^+ to make the resulting solution acidic. [1] explanation

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- (iii) Explain why an excess of water must be *very carefully added* to PCl_5 and PCl_3 .

[1]

The reactions are exothermic. [1]

- (iv) It is assumed that H_3PO_4 and H_3PO_3 behave as *dibasic (diprotic) strong acids*. Define the terms in italics, using H_3PO_4 as an example.

[2]

H_3PO_4 is a proton donor. One mole of H_3PO_4 ionises completely in water to produce 2 moles of H_3O^+ . [2] define strong + diprotic + acid

- (v) Determine, in terms of x , the number of moles of H^+ that will be formed after the addition of water to the mixture of PCl_5 and PCl_3 .

[4]

Amount / mol	PCl_5	\square	PCl_3	+	Cl_2
Initial	1		0		0
Change	$-x$		$+x$		$+x$
Eqm [1]	$1-x$		x		x

- $\text{PCl}_5 + 4\text{H}_2\text{O} \rightarrow 5\text{HCl} + \text{H}_3\text{PO}_4$
 $n(\text{H}^+) = n(\text{HCl}) = 5n(\text{PCl}_5) = 5(1-x) \text{ mol}$
 $n(\text{H}^+) = 2n(\text{H}_3\text{PO}_4) = 2(1-x) \text{ mol}$
 total $n(\text{H}^+)$ from $\text{PCl}_5 = 7(1-x) \text{ mol}$

- $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{HCl} + \text{H}_3\text{PO}_3$
 total $n(\text{H}^+)$ from $\text{PCl}_3 = 3x + 2x = 5x \text{ mol}$

[1] $n(\text{H}^+) = 2n(\text{diprotic acid})$, allow ECF from ICE table

[1] $n(\text{H}^+) = n(\text{PCl}_5 / \text{PCl}_3)$, allow ECF from ICE table

- total $n(\text{H}^+) = 7(1-x) + 5x = (7-2x) \text{ mol}$ [1] final ans. (no ECF)

The resulting solution was made up to 1.00 dm^3 in a standard flask. 25.0 cm^3 of this solution was titrated with $4.00 \text{ mol dm}^{-3} \text{ NaOH}$ and required 37.4 cm^3 for neutralisation.

- (f)(i) Calculate the total amount, in moles, of H^+ ions present in the 1.00 dm^3 standard flask.

[2]

$$n(\text{H}^+) \text{ in } 25.0 \text{ cm}^3 = n(\text{NaOH}) = 4.00 \times \frac{37.4}{1000} = 0.1496 \text{ mol [1]}$$

$$n(\text{H}^+) \text{ in } 1.00 \text{ dm}^3 = 0.1496 \times \frac{1000}{25.0} = 5.984 \text{ mol [1]}$$

- (ii) Using your answers to **(e)(v)** and **(f)(i)** to calculate the amounts, in moles of PCl_5 , PCl_3 and Cl_2 in the original equilibrium at 500 K.

[2]

$$7 - 2x = 5.984$$

$$x = 0.508 \quad [1] \text{ ECF from (e)(v) and (f)(i)}$$

[0] if $x > 1$

At equilibrium,

$$n(\text{PCl}_5) = 1 - 0.508 = 0.492 \text{ mol}$$

$$n(\text{PCl}_3) = 0.508 \text{ mol}$$

$$n(\text{Cl}_2) = 0.508 \text{ mol} \quad [1] \text{ all 3 eqm amounts, ECF from x value}$$

- (iii) Use your answer to **(d)** and **(f)(ii)** to calculate a value for K_c for the equilibrium.

[2]

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.508/5)^2}{(0.492/5)} \quad [1] \text{ convert amounts into concentrations}$$

allow ECF from **(d)** and **(f)(ii)**

$$= 1.066 \quad [1]$$

Section B

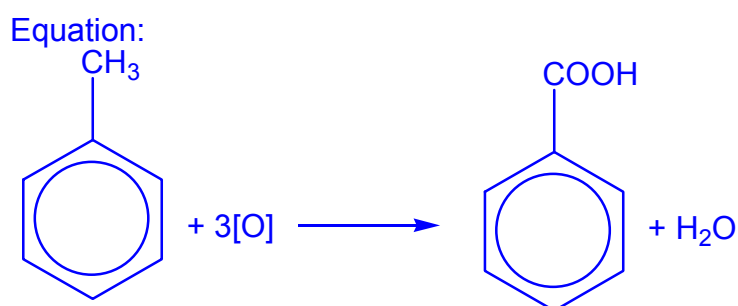
Answer **two** questions in this section on the writing paper provided.

- 1(a) Benzoic acid is a colourless crystalline solid. Salts of benzoic acid are used as food preservatives. The salts can be prepared by reacting benzoic acid with either sodium metal or sodium hydroxide.

- (i) Benzoic acid can be prepared from methylbenzene.

Write a balanced equation for this reaction, state the reagents and conditions necessary and name the type of reaction occurring. (In this equation the symbol [O] is acceptable.)

[3]



Reagents and conditions: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat [1]

Type of reaction: oxidation [1]

- (ii) State the type of reaction when benzoic acid reacts with sodium metal.

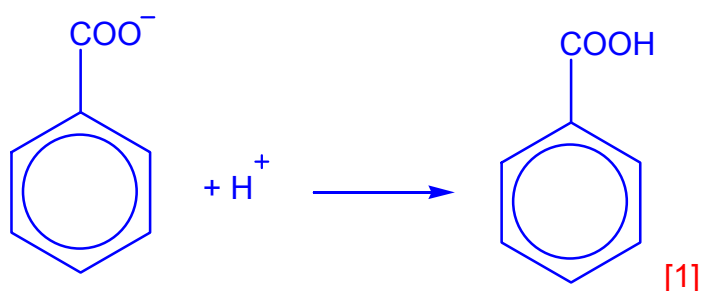
[1]

Reduction [1]

- (b)(i) When sodium hydroxide is added to benzoic acid, a buffer solution may be formed.

With an aid of an equation, explain how this buffer solution behaves when a small amount of acid is added to it.

[2]



When a small amount of acid is added to the buffer solution, the added H^+ ions are removed by reacting with the large reservoir of benzoate conjugate base. [1]

- (ii) Calculate the pH of 25.0 cm³ benzoic acid solution where the hydrogen ion concentration, [H⁺(aq)], is 0.025 mol dm⁻³.

[1]

$$\text{pH} = -\lg (0.025) = 2.90 \text{ [1]}$$

- (iii) Calculate the end point volume of 0.05 mol dm⁻³ sodium hydroxide when added to the solution in (b)(ii).

[1]

$$n(\text{NaOH}) = n(\text{H}^+) = \frac{25.0}{1000} \times 0.025 = 6.25 \times 10^{-4} \text{ mol}$$

$$V(\text{NaOH}) = \frac{6.25 \times 10^{-4}}{0.05} \times 1000 = 12.5 \text{ cm}^3 \text{ [1]}$$

- (iv) The table below shows the pH range of colour change for two acid-base indicators.

indicator	pH range of colour change
bromocresol-green	3.8 – 5.5
phenol-red	6.8 – 8.5

Suggest which indicator in the table above is a suitable indicator when benzoic acid is titrated against sodium hydroxide, explaining your answer.

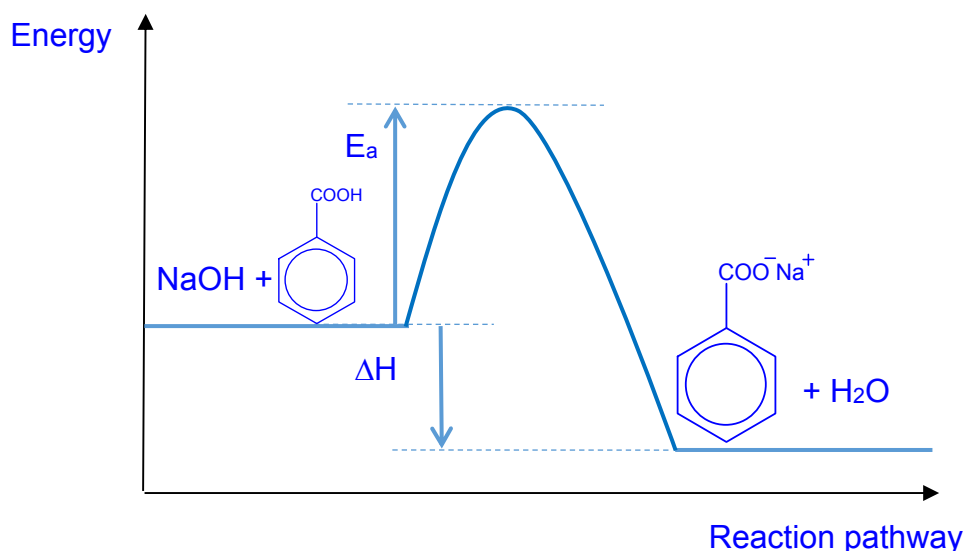
[2]

Phenol-red.[1]

The pH range of colour change of phenol-red (6.8 – 8.5) falls within the pH change at equivalence point (7 – 11). [1]

- (v) Draw a labelled reaction pathway diagram for the reaction between sodium hydroxide and benzoic acid.

[2]



[1] for labelling of y and x axes, E_{a1} , E_{a2} , reactants, intermediate and product (can ecf from part d)

[1] ΔH is exothermic

(vi) Suggest and explain the effect on the rate of the reaction of

- (I) an increase in concentration of benzoic acid,
- (II) a decrease in temperature of the solutions.

[3]

(I) When the [benzoic acid] increases, the benzoic acid molecules are closer to one another. The frequency of effective collisions increases, hence the rate of reaction increases. [1]

(II) A decrease in temperature will lead to a decrease in the average kinetic energy of benzoic acid molecules. Fewer molecules will have energies equal to or larger than E_a . [1] The frequency of effective collisions decreases, hence the rate of reaction decreases. [1]

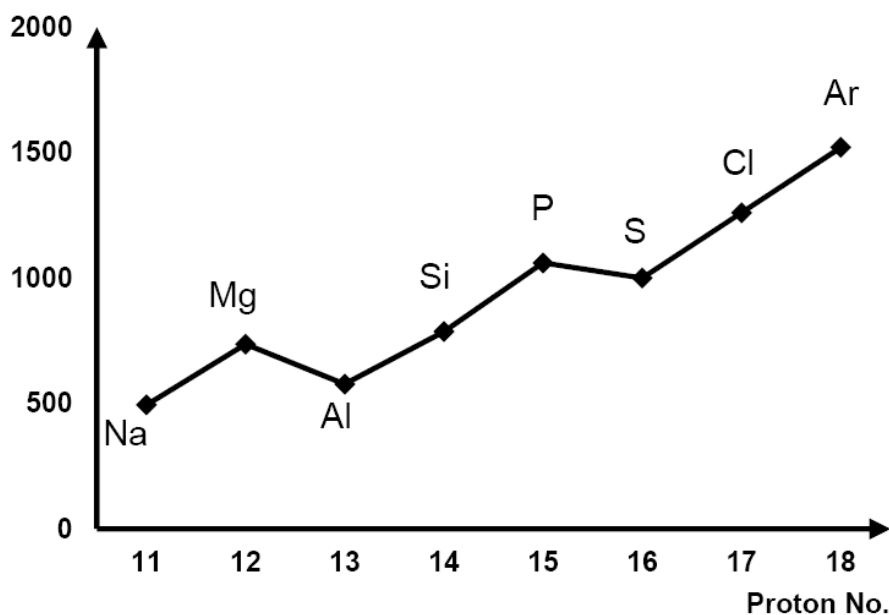
(c)(i) Define the first *ionisation energy* of sodium.

[1]

The first ionisation energy of sodium is the energy absorbed when one mole of electrons is removed from one mole of gaseous Na atoms to form one mole of singly-charged gaseous Na^+ . [1]

(ii) Sketch a graph to show the variation of the first ionisation energies of elements across the third period from Na to Ar.

[2]



General increasing trend [1]; Exceptions at Al and S [1]

- (iii) Explain the variation to the first ionisation energies you have illustrated in your sketch in part (ii). [2]

Across the third period, nuclear charge increases but shielding remains approximately constant as electrons are added to the valence shell. Net attraction of the nucleus for valence electrons increase, hence 1st IE generally increases as more energy is required to remove electrons. [1]

Mg ($1s^2 2s^2 2p^6 3s^2$) → Al ($1s^2 2s^2 2p^6 3s^2 3p^1$)

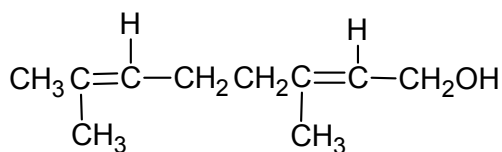
Al has a lower 1st IE than Mg as less energy is required to remove the 3p electron in Al as it experiences extra shielding by the filled 3s subshell.

P ($1s^2 2s^2 2p^6 3s^2 3p^3$) → S ($1s^2 2s^2 2p^6 3s^2 3p^4$)

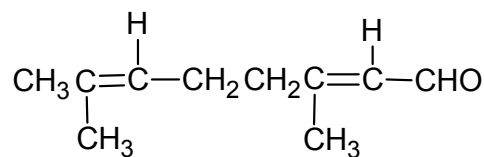
S has a lower 1st IE than P as less energy is required to remove the paired 3p_x electron in S as it experiences inter-electron repulsion. [1 for both]

[Total: 20]

- 2 Many of the natural compounds which are responsible for aromas in perfumes were first extracted from plants. Geraniol and citral, with the structures shown below, are found in roses and lemon grass and are attractants for honey bees.

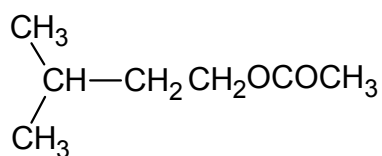


Geraniol



Citral

Banana oil is a bee alarm pheromone which is released during bee stings to attract other bees and provoke them to sting. Banana oil also have an odour similar to the smell of bananas.

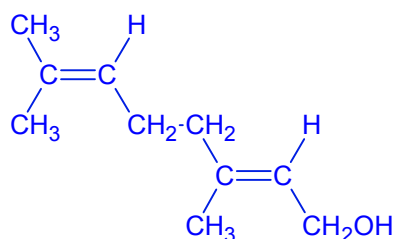


Banana oil

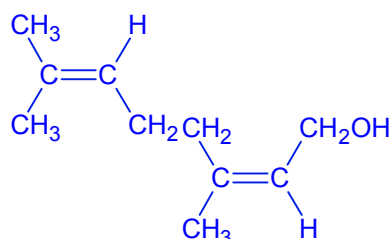
- (a) Identify the type of isomerism present in geraniol, and draw the structural formulae to illustrate the isomerism.

[3]

Cis-trans isomerism/Geometric isomerism [1]



Trans-isomer



cis-isomer

[1] cis-isomer

[1] trans-isomer

- (b)(i) What type of reaction is required to convert geraniol to citral? Suggest reagents and conditions for this reaction.

[2]

Oxidation. [1]

$\text{K}_2\text{Cr}_2\text{O}_7$ (aq), H_2SO_4 (aq), heat with distillation [1]

- (ii) Suggest a simple chemical test to distinguish between geraniol and citral.

[2]

Reagent: 2,4-dinitrophenylhydrazine, warm

Observations: orange ppt observed for Citral. No ppt for Geraniol

OR

Reagent: Fehling's reagent Warm

Observations: Brick-red ppt seen for Citral. No ppt seen for Geraniol

OR

Reagent: Tollen's solution. Warm.

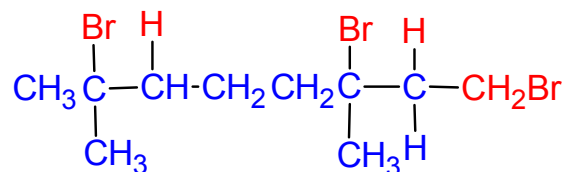
Observations: Ag mirror seen for Citral. No mirror seen for Geraniol

[1] reagents and condition

[1] observations

- (iii) Draw the structure of the organic product when geraniol is heated under reflux with HBr.

[2]



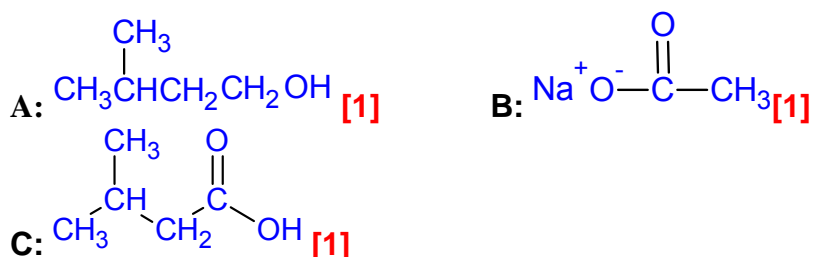
[1] addition of HBr across both double bonds & applies markovnikov rule

[1] substitution of ROH

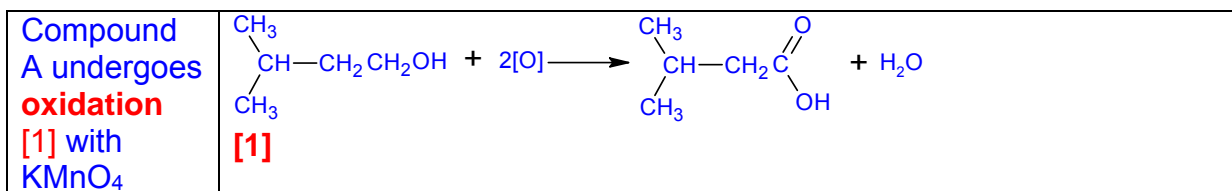
- (c) When banana oil is refluxed with aqueous NaOH, a slow reaction takes place to give compounds **A** and **B**. When compound **A** and **B** react with PCl₅ separately, compound **A** gives steamy white fumes but not compound **B**. Compound **A** forms compound **C** with the molecular formula, C₅H₁₀O₂ when heated with acidified KMnO₄.

- (i) Identify the structural formula of compounds **A**, **B** and **C**. State the type of reaction that have undergone and write balanced equations for all reactions that occurs.

[9]



Type of reaction	Equation
Banana Oil undergoes alkaline hydrolysis [1] with NaOH	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH} - \text{CH}_2\text{CH}_2\text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} + \text{NaOH} \longrightarrow \begin{array}{c} \text{CH}_3 \\ \\ \text{CH} - \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array} + \text{Na}^+ \text{O}^- - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3 $ [1]
Compound A undergoes substitution [1] with PCl ₅	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH} - \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array} + \text{PCl}_5 \longrightarrow \begin{array}{c} \text{CH}_3 \\ \\ \text{CH} - \text{CH}_2\text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array} + \text{POCl}_3 + \text{HCl} $ [1]



- (ii) Compound **C** has a boiling point of 176 °C whereas banana oil has a boiling point of 142 °C. With reference to the structures and type of bonding present in both compounds, explain why compound **C** has a higher boiling point than banana oil.

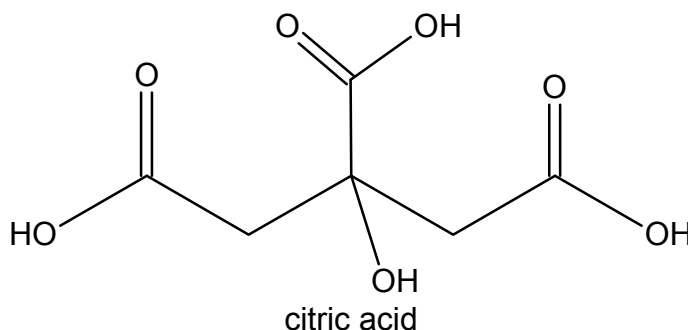
[2]

Both compound C and banana oil have simple molecular structures with weak intermolecular forces of attraction between molecules. **[1] -Structure**
Compound C has a higher boiling point despite having a smaller electron cloud because it can **form hydrogen bonding between molecules** whereas **banana oil only contains weak dispersion forces between molecules**.

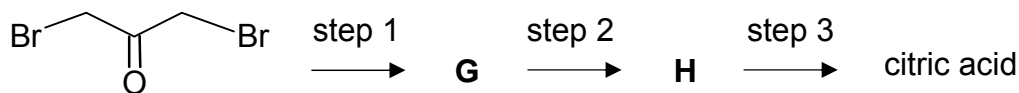
[1] -H bondings and dispersion forces

[Total: 20]

- 3 Citric acid, $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ occurs in lemons and limes. It is often used as a flavouring and preservative in food and beverages.



- (a) Suggest the reagents and conditions you would use in a three-step synthesis of citric acid from 1,3-dibromopropan-2-one, identifying the intermediates **G** and **H**.



[5]



step 1: ethanolic NaCN, heat under reflux **[1]**

step 2: HCN, trace amount of NaCN/HCN, 10-20 °C [1]

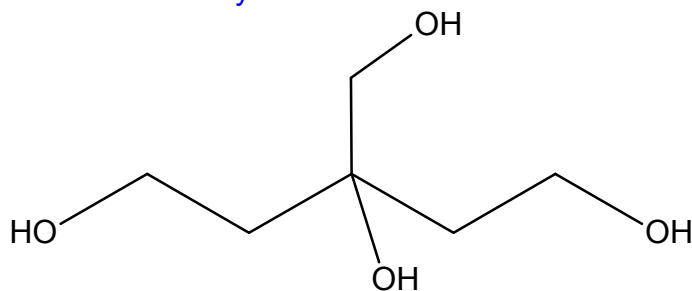
step 3: HCl(aq), heat [1]

intermediates **G** and **H** can be reversed and step 1 and 2 can be reversed.

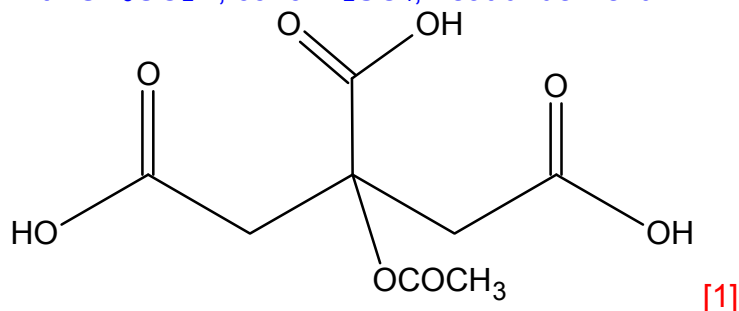
- (b) (i) Draw the structural formulae of the compounds formed when citric acid is treated with

- LiAlH_4 in dry ether,
- $\text{CH}_3\text{CO}_2\text{H}$, conc. H_2SO_4 , heat under reflux,
- Al_2O_3 , 350°C.

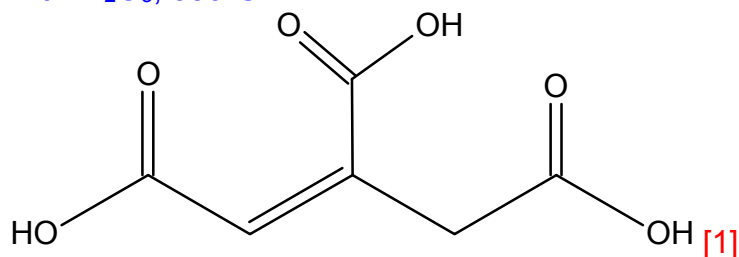
with LiAlH_4 in dry ether



with $\text{CH}_3\text{CO}_2\text{H}$, conc. H_2SO_4 , heat under reflux



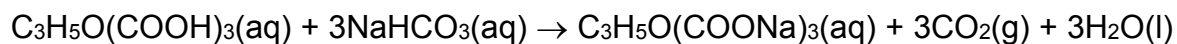
with Al_2O_3 , 350°C



- (ii) State the number of mole(s) of $\text{H}_2(\text{g})$ produced when 1 mole of citric acid is treated with Na.

2 [1]

- (c) The enthalpy change of neutralisation of citric acid by sodium hydrogencarbonate, NaHCO_3 , was determined experimentally by mixing known volumes of $0.20 \text{ mol dm}^{-3} \text{ C}_3\text{H}_5\text{O}(\text{COOH})_3(\text{aq})$ and $1.00 \text{ mol dm}^{-3} \text{ NaHCO}_3(\text{aq})$.



The following results were obtained.

volume of $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3(\text{aq})$ used	= 50 cm^3
volume of $\text{NaHCO}_3(\text{aq})$ used	= 50 cm^3
change in temperature	= - 0.5 $^\circ\text{C}$

- (i) Define the term *standard enthalpy change of neutralisation*.

[1]

energy change/released when 1 mole of water is produced from the neutralisation of an acid with a base. [1]

- (ii) Use the data above to determine, by calculation, which reactant, $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ or NaHCO_3 is in excess.

[2]

$$n(\text{C}_3\text{H}_5\text{O}(\text{COOH})_3) = 50/1000 \times 0.20 = 0.01 \text{ mol}$$

$$n(\text{NaHCO}_3) = 50/1000 \times 1.0 = 0.05 \text{ mol}$$

If $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ is the limiting reagent, $n(\text{NaHCO}_3)$ needed for the reaction = $0.01 \times 3 = 0.03 \text{ mol}$ which is less than the given $n(\text{NaHCO}_3)$. [1]

Hence NaHCO_3 is in excess. [1]

- (iii) Hence, calculate the standard enthalpy change of neutralisation of citric acid by NaHCO_3 .

[3]

$$n(\text{H}_2\text{O}) = 0.01 \times 3 = 0.03 \text{ mol}$$

$$\Delta H_{\text{neut}} = + \frac{100 \times \frac{4.18}{1000} \times 0.5}{0.03} = +6.97 \text{ kJ mol}^{-1}$$

1 mark for calculating the amount of water produced

1 mark for applying the formula correctly

1 mark for indicating the positive sign and giving the correct numerical value and units

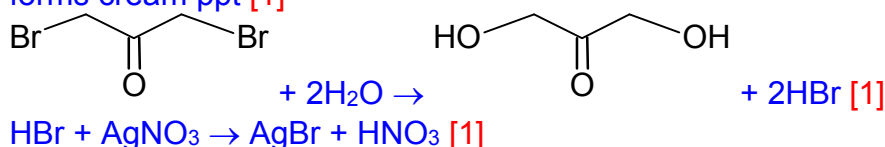
- (d) 1,3-dibromopropan-2-one undergoes hydrolysis with the water present in silver nitrate solution.

- (i) Describe how this reaction could be used to distinguish between 1,3-dibromopropan-2-one and 1,3-dichloropropan-2-one, including all observations that would be made. Write relevant equations using 1,3-dibromopropan-2-one as your example.

[3]

1,3-dibromopropan-2-one and 1,3-dichloropropan-2-one can be identified based on colour of precipitate formed.

1,3-dichloropropan-2-one forms white ppt and 1,3-dibromopropan-2-one forms cream ppt [1]



- (ii) Explain the difference in reactivities between 1,3-dibromopropan-2-one and 1,3-dichloropropan-2-one.

[2]

The atomic radius of bromine atom is longer than the atomic radius of chlorine atom. Hence the C-Br bond is shorter than the C-Cl bond. Since the C-Br bond is easier to break [1], 1,3-dibromopropan-2-one will react faster with the water present in silver nitrate solution and the cream ppt will appear faster [1].

[Total: 20]

End of Paper