



Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE
NAME

CLASS

2T

CHEMISTRY

9729/02

Paper 2 Structured Questions

Friday 17 August 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of 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				%
Paper 1			30	15
Paper 2	Q 1	15		
	Q 2	15		
	Q 3	15		
	Q 4	15		
	Q 5	15	75	30
Paper 3	Q 1	20		
	Q 2	20		
	Q 3	20		
	Q 4 / 5	20	80	35
Paper 4			55	20
Total % and Grade				100

This document consists of **18** printed pages.

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

- 1** In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.
- (a)** In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4 . The decomposition of N_2O_5 was found to be a first-order reaction.



Table 1.1 below shows the variation of $[\text{N}_2\text{O}_5]$ with time.

Time / s	$[\text{N}_2\text{O}_5] / \text{mol dm}^{-3}$	$\ln [\text{N}_2\text{O}_5]$
0	0.910	
300	0.750	
600	0.640	
1200	0.440	
3000	0.160	

Table 1.1

- (i)** State the rate equation for the decomposition of N_2O_5 .

..... [1]

- (ii)** The rate equation for the decomposition of N_2O_5 can also be expressed as:

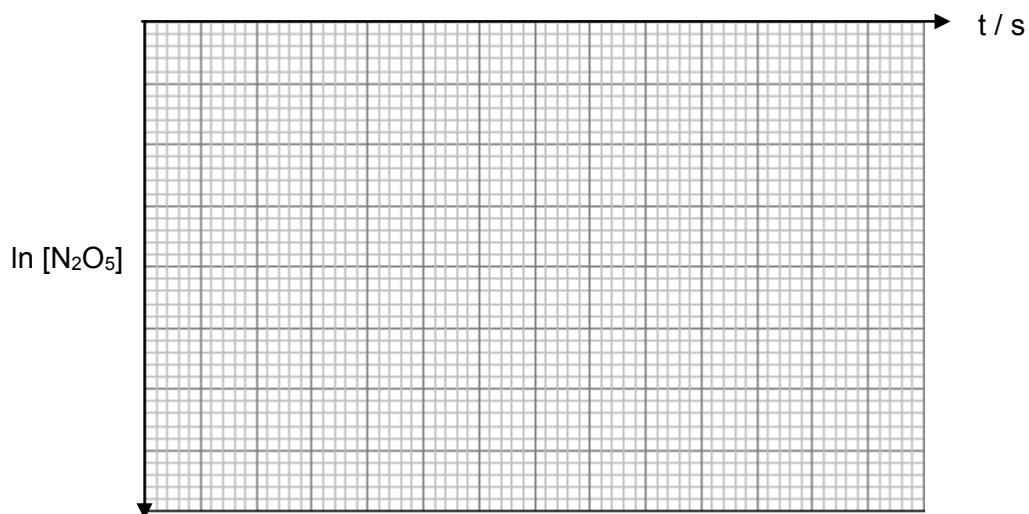
$$\ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_0$$

where $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 and $[\text{N}_2\text{O}_5]_t$ is the concentration of N_2O_5 at time, t .

Using relevant data in Table 1.1, calculate the values for $\ln [\text{N}_2\text{O}_5]$ and complete Table 1.1.

[1]

- (iii) Using the following axes and relevant data in Table 1.1, plot a graph of $\ln [\text{N}_2\text{O}_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

- (iv) Using your graph, determine a value for the rate constant, k , for the decomposition of N_2O_5 . State the units of k clearly.

[2]

- (v) Hence determine a value for the half-life of the decomposition of N_2O_5 . State the units clearly.

[1]

- (vi) Outline another experiment to determine the rate constant, k , for the decomposition of N_2O_5 in tetrachloromethane.

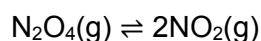
You are provided with the same solution of N_2O_5 used in the experiment described in (a).

No details regarding use of specific glassware are required.

.....

 [2]

- (b) The NO_2 produced in the decomposition reaction in (a) can exist in equilibrium with dinitrogen tetroxide (N_2O_4):



An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm ⁻³		Equilibrium concentration / mol dm ⁻³	
	[N_2O_4]	[NO_2]	[N_2O_4]	[NO_2]
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

- (i) State *Le Chatelier's Principle*.

.....

 [1]

- (ii) State what will be observed when the pressure in the reaction vessel is decreased.

.....
 [1]

- (iii) Identify the experiment that gives the initial concentration of N_2O_4 : NO_2 in the ratio 15:1.

..... [1]

- (iv) Based on the experiment identified in (b)(iii), calculate a value for the equilibrium constant, K_c .

[1]

- (v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined.

K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in (b)(iv) and the above expression, calculate a value for the K_p for the reversible reaction between N_2O_4 and NO_2 .

[2]

[Total: 15]

- 2 (a) Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

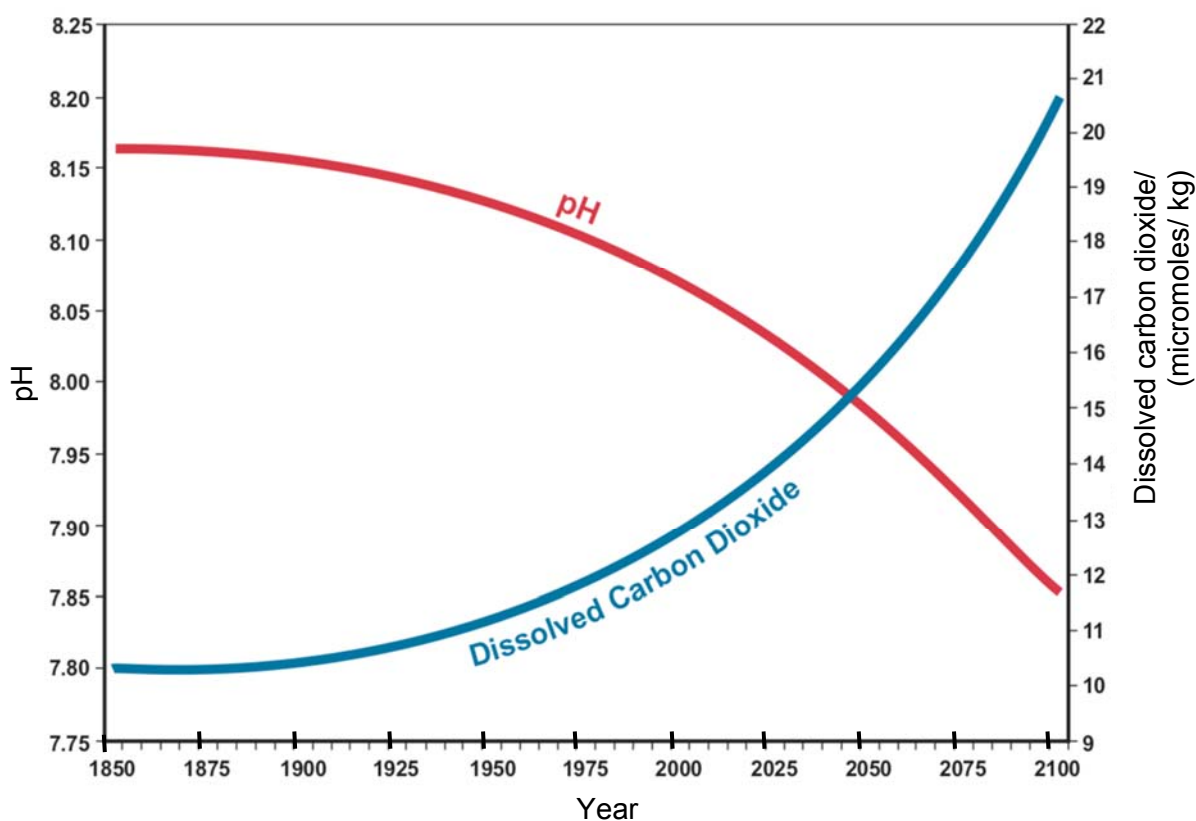
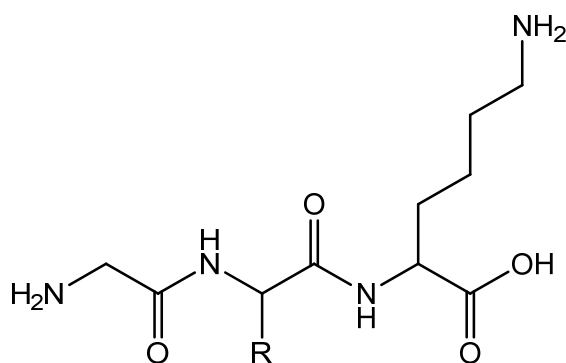


Fig. 2

- (i) State what is meant by a *zwitterion*.
 [1]
- (ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

 [1]
- (iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO_2 .
 [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.



GHK

- (iv) Circle any chiral carbon atom on the above structure, GHK. [1]
- (v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.

[2]

- (vi) Use the graph in Fig. 2 to determine from which year onwards, more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

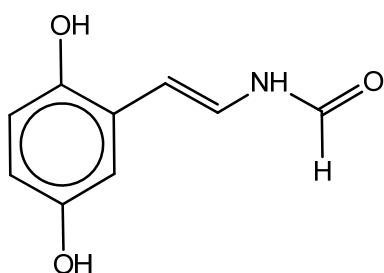
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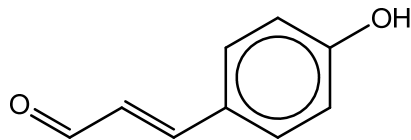
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..... [2]

- (b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin



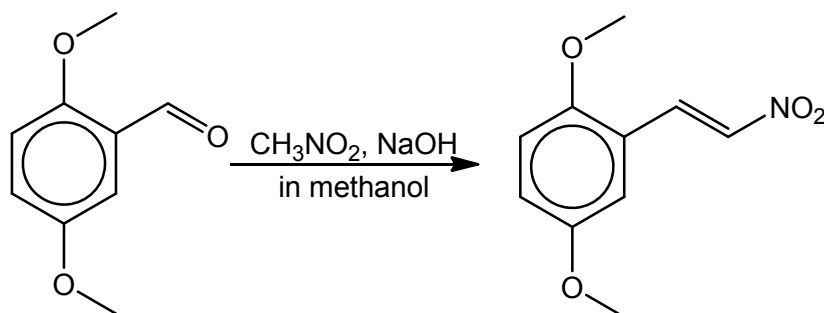
4-hydroxy cinnamaldehyde

- (i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

.....

 [3]

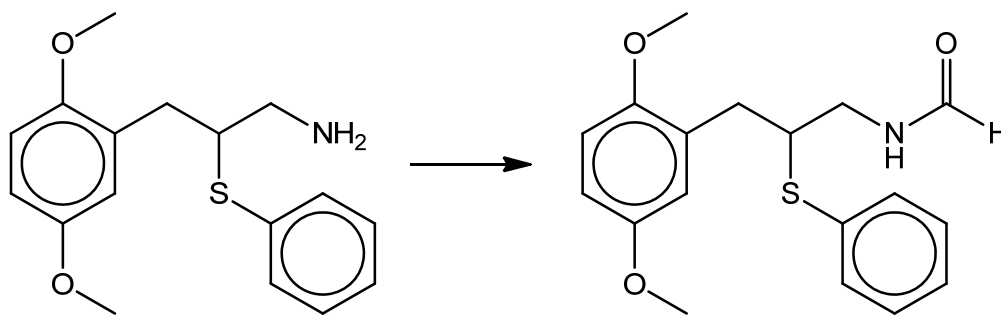
The synthesis of erbstatin involved the following step.



- (ii) Given that NaOH is used as a base to form $^-\text{CH}_2\text{NO}_2$ as a nucleophile, suggest the type of reaction in the above step.

..... [1]

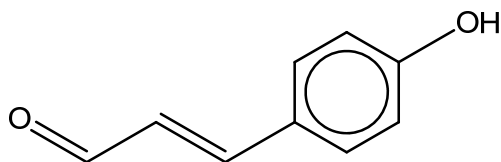
Another step in the synthesis of erbatin is shown below.



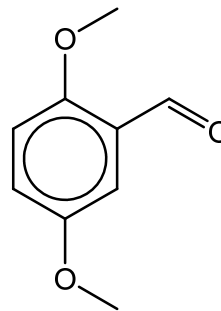
(iii) Suggest suitable reagents for the above step.

..... [1]

(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

.....

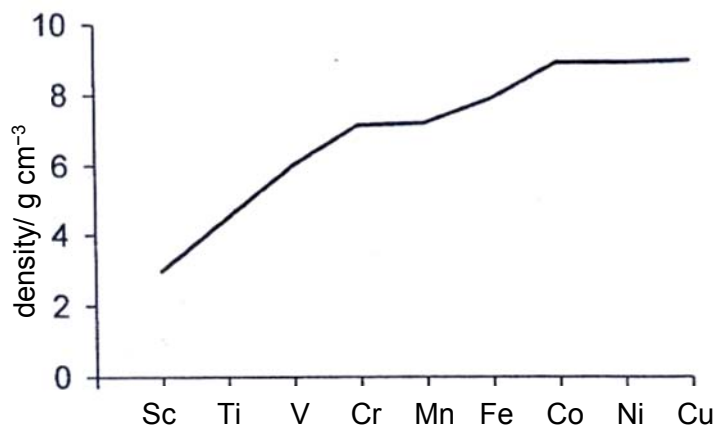
 [2]

[Total: 15]

- 3 (a) d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

The graph below shows the densities of the elements Sc to Cu.

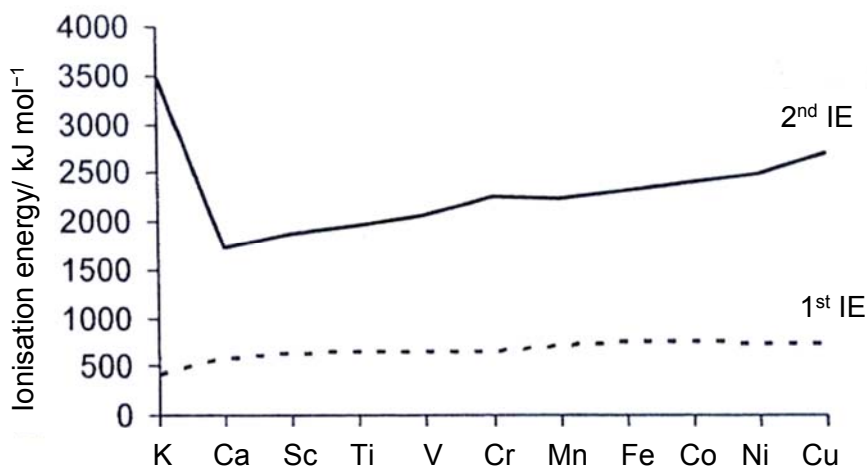


- (i) Suggest why the densities of the elements increase from Sc to Cu.

.....

 [2]

- (ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

.....

 [2]

- (iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

.....
 [1]

- (b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

- (i) Define the term *transition element*.

.....
 [1]

- (ii) State the full electronic configuration of Sc^{3+} .

.....[1]

- (iii) Explain why scandium is not classified as a transition element.

.....
 [1]

- (c) X and Y are period 3 elements.

Element X forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element Y forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element Y is added to the oxide of element X with water.

Identify the elements X, Y, and the oxide of Y.

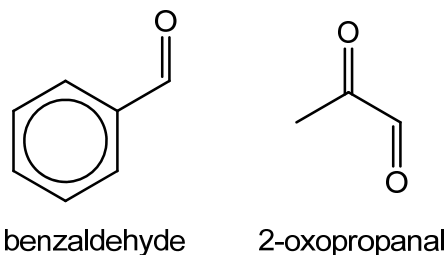
Explain the observations with the aid of relevant equations.

.....

 [7]

[Total: 15]

- 4 (a) Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



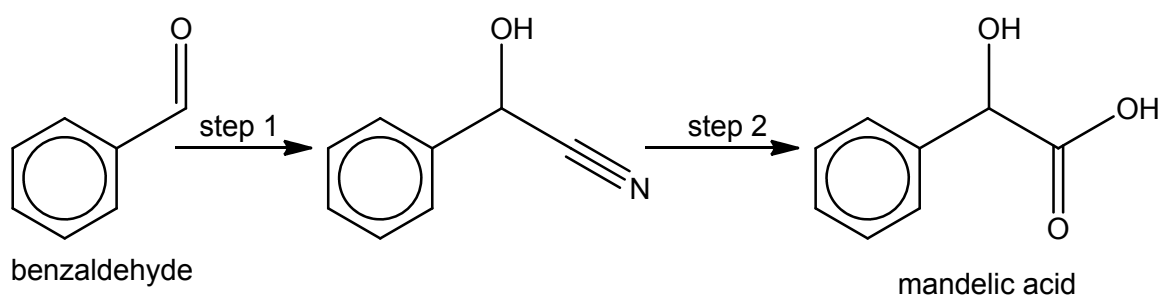
- (i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions:

	Observations:	Products:
benzaldehyde		
2-oxopropanal		

[3]

- (ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



State the reagents and conditions for steps 1 and 2.

Step 1:

Step 2:

[2]

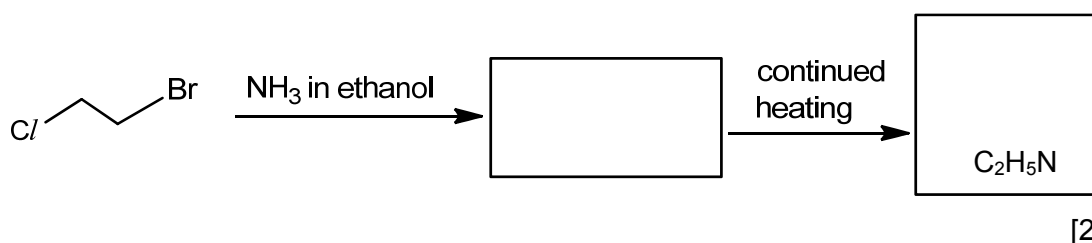
(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

- (i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

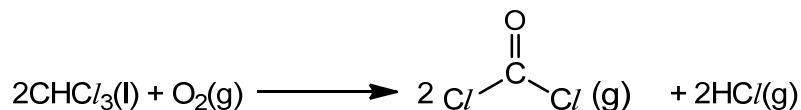
.....

 [1]

- (ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



- (c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, COCl_2 . This reaction can also take place slowly in the presence of oxygen and light, as represented below.



- (i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $\text{CHCl}_3(\text{l})$ is $+31 \text{ kJ mol}^{-1}$.

[3]

- (ii) Predict, with reasons, the sign of the entropy change of the reaction in (c)(i).

.....

 [2]

- (iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

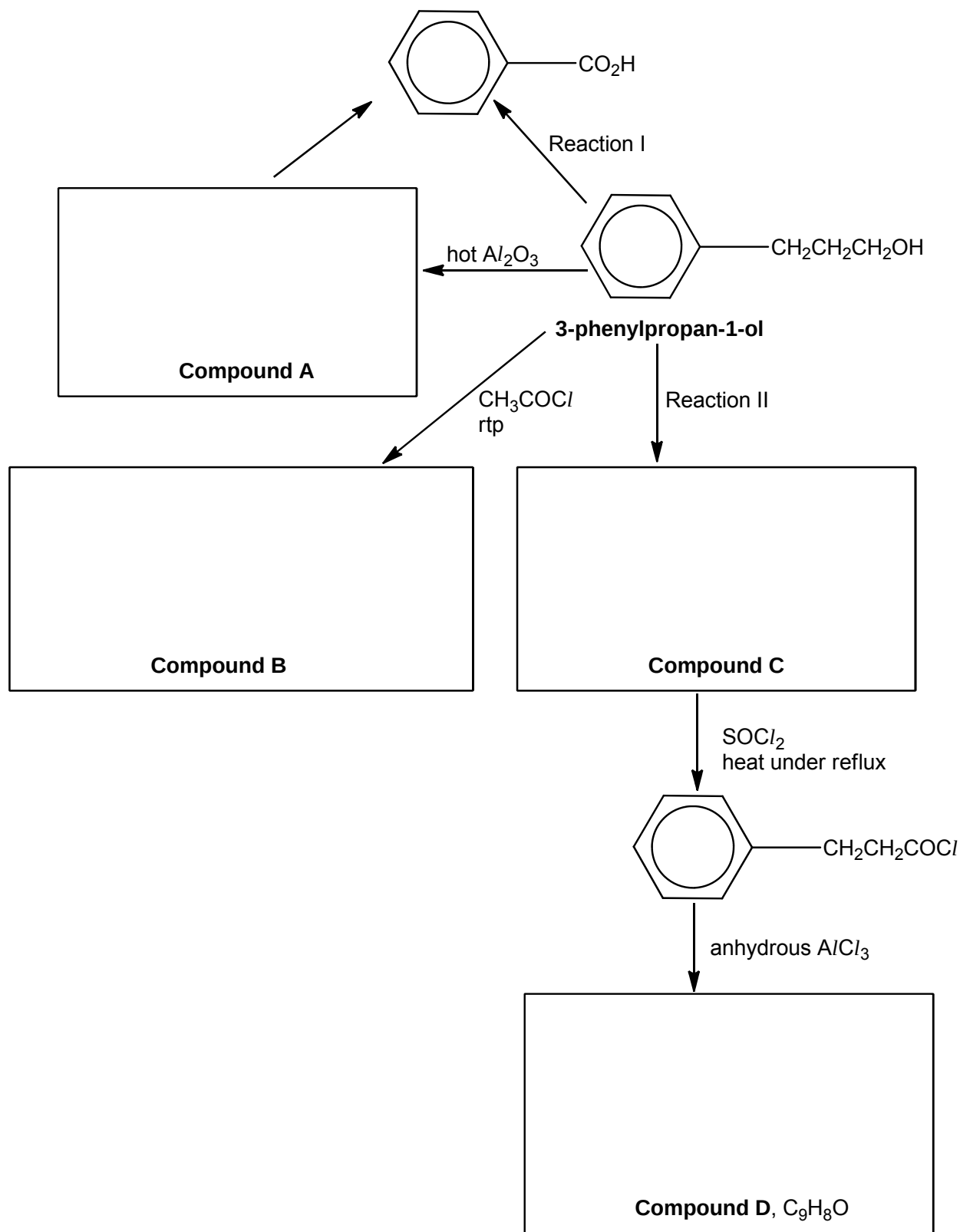
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 [2]

[Total: 15]

- 5 (a) Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

- (i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

- (ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II.

Reaction I

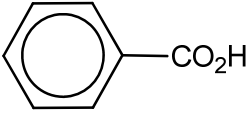
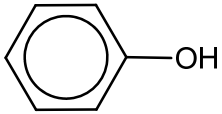
Reaction II

[2]

- (b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	structural formula	$K_a / \text{mol dm}^{-3}$
benzoic acid		6.3×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

- (i) Draw the organic product formed when CO_2 is bubbled through a solution of aqueous sodium phenoxide.

[1]

- (ii) However, no reaction occurs when CO_2 is bubbled through a solution of aqueous sodium benzoate. Explain why this is so.

.....

.....

.....

..... [1]

- (c)** Cumene, C_9H_{12} , is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** separately under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

- (i) State reagent **W**.

.....[1]

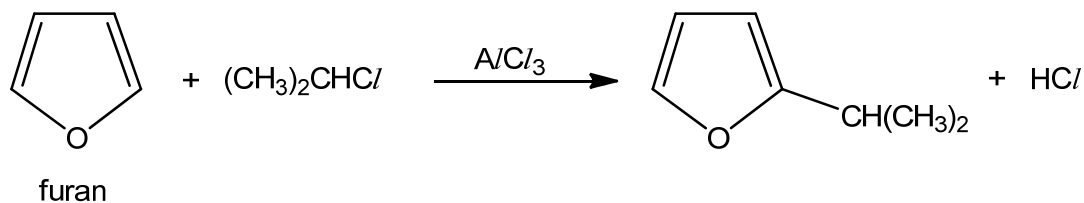
- (ii) In the space below, give the structural formula of compound X, Y and Z.

Compound X	Compound Y	Compound Z

[3]

- (d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

Outline the mechanism of the reaction below, clearly showing all the steps involved.



[3]

[Total: 15]