CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9647/02
Paper 2 Structured Questions
TUESDAY 13 SEPTEMBER 2011
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 on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided
You are reminded of the need for good English and clear presentation in your answers.

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

ANSWERS

1 Planning (P)

A mixture of sodium carbonate, Na_2CO_3 and sodium hydrogencarbonate, $NaHCO_3$ is heated strongly with a bunsen burner. ***Only*** sodium hydrogencarbonate, $NaHCO_3$ decomposes on heating.

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

You are to design an experiment to determine the percentage by mass of sodium hydrogencarbonate, $NaHCO_3$ in a 5.00 g sample of a mixture of sodium carbonate, Na_2CO_3 and sodium hydrogencarbonate, $NaHCO_3$, by ***heating*** alone.

The only apparatus available consists of a boiling-tube and holder, a heat-proof mat, a chemical balance and a bunsen burner.

(a) Outline step by step, the practical sequence for the method you would use to

- make appropriate weighings,
- decompose $NaHCO_3$ in the sample by heating,
- ensure that decomposition was complete.

Weigh accurately the empty **dry** boiling-tube, using a chemical/electronic balance.

Add 3.00 g of the mixture of the sample and weigh the boiling-tube and contents (or any reasonable ***specified*** amount).

Heat the sample in the boiling-tube **strongly**, for about 5 minutes, using a test-tube holder and bunsen burner.

Allow the boiling-tube and the contents to cool on a heat-proof mat.

After cooling, reweigh the boiling-tube and its contents.

Repeat the heating, cooling and reweighing until there is **no further loss** in mass. This is to ensure that all the $NaHCO_3$ has decomposed completely.

[4]

(b) Show how you would tabulate your results. Include in your table and other masses you would calculate from the experimental results to enable you to determine the percentage by mass of $NaHCO_3$ in the sample of the mixture. Insert in your table, the letters **A**, **B**, **C** etc. to represent each measurement of mass.

Mass of boiling-tube and sample/g	B
Mass of empty boiling-tube/g	A
Mass of sample/g	B - A
Mass of boiling-tube and contents/g **after 1st heating**/g **after 2nd heating**/g	C C(showing constant mass)
Loss in mass/g	B - C

[3]

(c) Use the letters you have entered in (b) to show how you would process the results to find

(i) the mass of $NaHCO_3$ in the sample of the mixture

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + \underbrace{CO_2(g) + H_2O(g)}_{(B - C)\ g}$$

m g (say)

Amount of $NaHCO_3 = \frac{m}{84}$ mol

Amount of CO_2 = amount of $H_2O = \frac{1}{2} \times \frac{m}{84} = \frac{m}{168}$ mol

$$\therefore \quad \frac{m}{168}(44.0) + \frac{m}{168}(18.0) = (B - C)\ g$$

$$\frac{62m}{168} = (B - C)$$

$$m = 2.71(B - C)\ g$$

(ii) the % by mass of $NaHCO_3$ in the sample of the mixture.

$$\% \text{ by mass of } NaHCO_3 = \frac{2.71(B-C)}{B-A} \times 100\ \%$$

[4]

(d) Suggest an alternative experimental method, ***not*** involving weighing, which could be used to determine the % by mass of $NaHCO_3$ in the sample of the mixture.

By heating the sample and collect (and measure) the ***volume of $CO_2(g)$*** liberated using a ***gas syringe*** at r.t.p, **OR**

By adding ***excess $H_2SO_4(aq)$/HCl(aq)*** to the sample and collect (and measure) the ***volume of $CO_2(g)$*** liberated using a ***gas syringe*** at r.t.p. **OR**

By titrating an aqueous solution of the sample with standard ***$H_2SO_4(aq)$/HCl(aq)*** by a double indicator method (phenolphthalein and methyl orange).

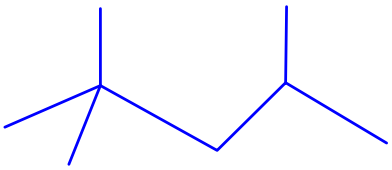
[1]

[Total: 12]

2 Most automobiles today are powered by internal combustion engine, where a certain fuel is used and burned with a mixture of air to produce useful energy. In Singapore, methane (marketed as compressed natural gas, CNG), has been actively promoted and used as an alternative fuel to petrol (contains mainly iso-octane). Biofuels such as methanol and ethanol have been considered viable alternative fuels as well. Some properties of the fuels are listed in the table below.

Types of Fuel	$\Delta H_c^{\ominus}$ Standard enthalpy change of combustion (kJ mol^{-1})	Boiling point (^oC)	Solubility in water (g/cm^3)
CH_4	−891	-161	35
iso-octane (C_8H_{18})	−5461	99	insoluble
CH_3OH	−726	60	very soluble
CH_3CH_2OH	−1300	74	very soluble

(a) Iso-octane has the IUPAC name 2,2,4-trimethylpentane. Draw the structural formula of iso-octane. (You may wish to use skeletal formula.)



[1]

(b) Boiling point is an important practical consideration when selecting fuel.

(i) Account for the difference in boiling point between iso-octane and methane.

Iso-octane is a larger molecule with a **larger electron cloud/number of electrons**, which results in **more extensive van der waal's forces of attraction** as compared to methane. Hence more energy is required to break the intermolecular forces of iso-octane during the boiling process.

(ii) Suggest a possible benefit of using petrol (iso-octane) compared to methane as fuel due to its boiling point.

Ease of storage or transport as octane is liquid at r.t.p, while methane is a gas.

[3]

(c) Another important factor for suitable alternative fuel is the amount of heat released which can be related to the standard enthalpy change of combustion, ΔH_c of the compound.

(i) Define the term standard enthalpy change of combustion.

The standard enthalpy change of combustion is defined as the enthalpy change when **one mole of a compound** is **completely** burnt in excess oxygen under standard conditions of **298K and 1 atm**.

(ii) From the data given in the table, ΔH_c of methanol is −726 kJ mol^{-1}. However, when the value is calculated from bond energy data, the ΔH_c of methanol is −886 kJ mol^{-1}. Account for the large difference in the values.

Bond energy is the energy required to break covalent bonds in the gaseous state, but at standard conditions, methanol and water exists as liquid.

(iii) With reference to the table, iso-octane releases the most energy. But for practical reasons, the most ideal fuel is best quantified by the highest energy released per unit mass. By considering this, state which fuel is most ideal and energy released per gram.

Fuel: CH_4 Energy evolved: 55.7 kJ g^{-1}

(iv) A common fear of installing CNG tank is the possible leakage and explosion of the methane gas. However, methane will only burn at 1200 K without any spark or ignition. Suggest the reason for the need of a high temperature.

Covalent bonds are strong and require a lot of energy to break; hence a high temperature is required to provide this energy.

[5]

(d) The use of combustion to generate energy results in undesirable and harmful gas released in the exhaust. Due to the nature of the fuel and insufficient oxygen in the air, incomplete combustion may occur. Furthermore, high temperature of the engine may cause reaction between normally unreactive gases like oxygen and nitrogen.

(i) State the gas released due to incomplete combustion of carbon-based fuel such as methane and its harmful effect at high concentration.

Carbon monoxide, which can cause blood-poisoning\suffocation at high concentration.

(ii) Alcohols have an advantage over hydrocarbons, as they have lower chances of incomplete combustion. Suggest why this is so from their molecular formulae.

Alcohols contain oxygen which can help to increase the oxygen content of the fuel-air mixture.

(iii) Production of nitrogen oxides can lead to an increase in greenhouse effect as well. Besides that, suggest another environmental impact of these oxides.

Acid rain\Photochemical Smog\Depletion of Ozone layer

[3]

(e) Water in the fuel is undesirable as its presence reduces the heat energy obtained from combustion as some energy is used to evaporate the water. Hence, identify which fuel is a poor choice due to this. Briefly explain your answer in terms of bonding.

Methanol\Ethanol which is very soluble in water, hence it can easily be contaminated with water. The high solubility is due to the favourable **hydrogen bonding** formed between water and methanol\ethanol. [2]

(f) The use of the fuel cells is an alternative method to power an automobile. The same chemical reaction occurs as that of the combustion between methane and oxygen, producing carbon dioxide and water. The useful energy generated for a fuel cell is the Gibbs free energy instead.

(i) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$ of methane, given that standard entropy change of combustion is -245 J K^{-1} mol^{-1}.

$\Delta G^{\ominus} = \Delta H - T\Delta S = -891 - 298\left(\frac{-245}{1000}\right) = -818$ kJ mol^{-1}

(ii) State the oxidation numbers of carbon in methane and carbon dioxide, and the number of electrons transferred in the reaction.

Methane: -4 Carbon dioxide: +4 Number of electrons: 8

(iii) $\Delta G^{\ominus}$ x 1000= -n$FE^{\ominus}$ is an equation that can relate $\Delta G^{\ominus}$ (in kJ mol^{-1}), and $E^{\ominus}$ (in V). By considering the answer in (ii) and given that n is the number of moles of electrons transferred while F is the Faraday constant, calculate the $E^{\ominus}$ for a methane/oxygen fuel cell.

$E^{\ominus} = \frac{-(-818 \times 1000)}{8(96500)} = +1.06$ V

[4]

[Total: 18]

3 Hydrobromic acid, HBr, is one of the strongest mineral acids known and is even stronger than hydrochloric acid. Both the industrial and laboratory syntheses of HBr are well documented due to the usefulness of HBr in many chemical reactions.

(a) The primary industrial preparation of HBr involves the platinum-catalysed reaction between hydrogen and bromine at temperatures between 450 – 700 K.

$$H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$$

The reaction was carried out in a 250 m^3 vessel at 607 K.

(i) Calculate the amount of HBr present at equilibrium, given that the equilibrium partial pressure of HBr is 2 atm.

$PV = nRT$

$n = \dfrac{PV}{RT}$

$n = \dfrac{(2 \times 101000)(250)}{8.31 \times 607}$

$n = 1.00 \times 10^4$ mol

At 607 K, the equilibrium constant, K_p, for the above reaction is 2.50.

(ii) Write the expression for the equilibrium constant, K_p, for the above reaction.#

$$K_p = \frac{(P_{HBr})^2}{P_{H_2} P_{Br_2}}$$

(iii) At equilibrium, the number of hydrogen molecules is ten times that of bromine molecules.

Calculate the amount of bromine present at equilibrium.

Let x be the number of moles of Br_2.

Number of moles of $H_2 = 10x$

$$K_p = \frac{(P_{HBr})^2}{P_{H_2} P_{Br_2}} = \frac{(1 \times 10^4)^2}{(10x)(x)} = 2.50$$

$x = 2 \times 10^3$ mol

(iv) Assuming that only hydrogen and bromine were present at the start of the reaction, hence determine the mass of bromine (in kg) required.

Since only hydrogen and bromine was present in the vessel in the beginning, all the hydrogen bromide formed must have come from Br_2 initially.

Initial no. of moles of Br_2
= No. of moles of Br_2 at equilibrium + ½ x no. of moles of HBr
= $2 \times 10^3 + ½ \times (1.00 \times 10^4)$
= 7.00×10^3 mol

Mass of $Br_2 = 7.00 \times 10^3 \times 79.9 \times 2$
= 1118kg

[7]

(b) The preparation of the acid, HBr in the laboratory can be carried out by the reaction between bromine, sulfur dioxide and water **only**. The only by-product formed is also a strong acid.

(i) Write the equation for the above laboratory preparation of HBr.

$Br_2 + SO_2 + 2\ H_2O \rightarrow 2\ HBr + H_2SO_4$

(ii) When concentrated solutions of the two products formed in the above preparation reacts with each other, Br_2 is regenerated. State and explain the type of reaction that is occurring.

Oxidation.

Concentrated sulfuric acid is an oxidizing agent and will oxidize HBr to Br_2.

[3]

(c) Another method of producing HBr in the laboratory is carried out by reacting sodium bromide with concentrated phosphoric(V) acid, H_3PO_4.

(i) Give the equation for the reaction between sodium bromide and concentrated phosphoric(V) acid.

$NaBr + H_3PO_4 \rightarrow HBr + NaH_2PO_4$

(ii) Suggest a reason why this method is preferred in the laboratory over the method described in part **(b)**.

H_3PO_4 does not oxidise HBr.

[2]

(d) Intra and intermolecular bondings can explain the trends in the thermal stability and boiling points of the hydrogen halides.

(i) State and explain the trend in the boiling points of hydrogen halides from HF to HI.

HC*l* to HI molecules: Increasing BP from HC*l* to HBr to HI,

HF molecules: HF boiling point is exceptionally high.

HC*l* to HI molecules: Increasing size of the halogen atom causes the size of the hydrogen halides to increase down the group, thus the van der Waals' forces of attraction increases down the group.

HF molecules: Due to hydrogen bonding between HF molecules, HF has an exceptionally high boiling point.

(ii) State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

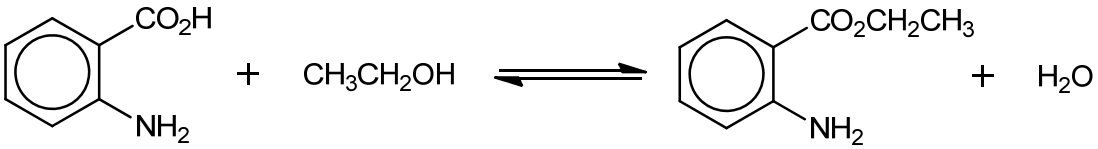
Decreasing stability of the hydrogen halides down the group. This is because down the group, the H-X bond becomes longer, the bond becomes weaker and the bond energy becomes lower ; the hydrogen halides will be broken down by heat more readily.

[6]

[Total: 18]

4 Ethyl 2-aminobenzoate is an ester that is commonly used as food flavouring to give it a grape smell. The ester can be synthesized by adding 2-aminobenzoic acid and ethanol in a round-bottom flask and heating it under reflux. At the end of the reaction, two immiscible layers are obtained.

The reaction between 2-aminobenzoic acid and ethanol is actually an equilibrium process. Concentrated sulfuric acid is added as a catalyst to help speed up the reaction.



2-aminobenzoic acid ethyl 2-aminobenzoate

(a) Apart from speeding up the reaction, suggest one other possible use for adding concentrated sulfuric acid.

Sulfuric acid is a dehydrating agent that removes water,thus pushing the position of equilibrium to the right. [1]

(b) By considering Le Chatelier's principle, suggest another possible method to increase the yield of the reaction.

Increase the amount of acid/alcohol used. [1]

(c) In addition to the products shown above, another organic by-product was formed. Identify the organic by-product formed and write an equation for its formation.

By-product: $CH_2=CH_2$ OR $CH_3CH_2OCH_2CH_3$

Equation:

$CH_3CH_2OH \longrightarrow CH_2=CH_2 + H_2O$

OR

$2\ CH_3CH_2OH \longrightarrow CH_3CH_2OCH_2CH_3 + H_2O$

[2]

(d) After the reaction, aqueous sodium hydroxide, which is a **strong** base, was added to the mixture of two immiscible layers to remove some impurities. The aqueous layer was discarded while the organic layer was heated and then distilled.

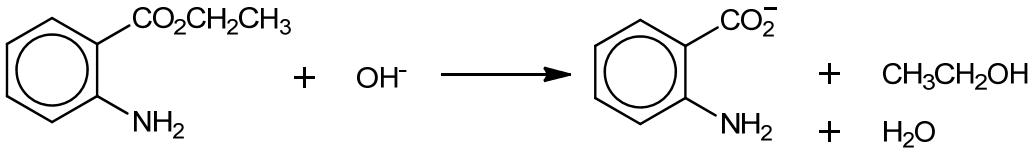
(i) Suggest the two species that are removed in the aqueous layer.

2-aminobenzoic acid, H_2SO_4 ……..

……

(ii) Explain with the use of an equation why a small amount of aqueous sodium hydroxide left in the organic layer would result in a lower yield of ester and state the type of reaction that is occurring.

Hydrolysis could have occurred in the presence of NaOH(aq).



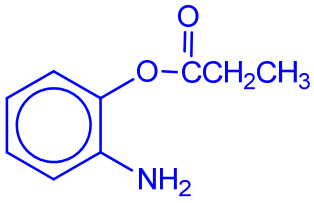
[4]

(e) Another ester, which is an isomer of ethyl 2-aminobenzoate, **cannot** be synthesized using the method described above.

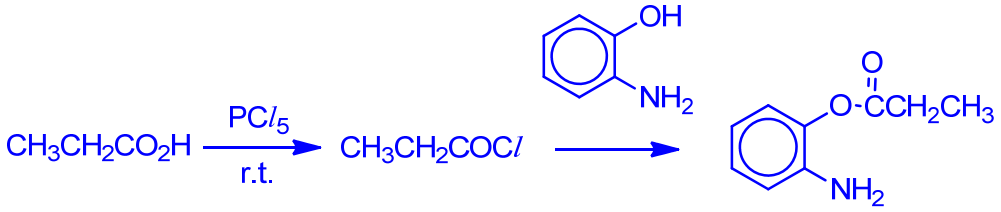
(i) State the type of isomerism and draw the structure of the isomer.

Type of isomerism: Structural isomerism ……..

Structure of isomer:



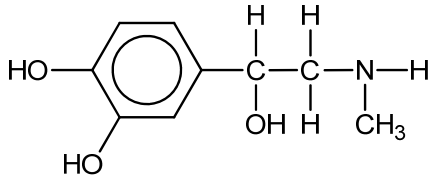
(ii) Hence, outline the synthesis for the ester drawn in **(e)(i)** starting from a suitable carboxylic acid.



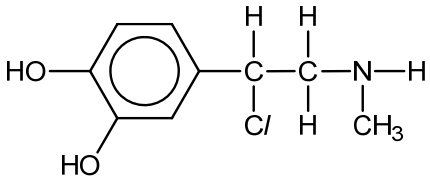
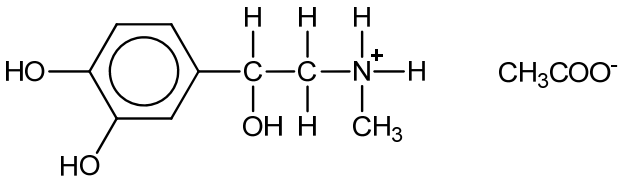
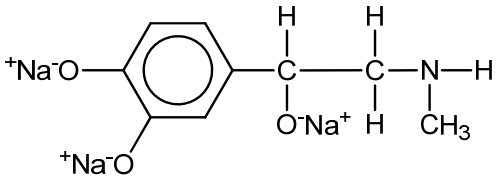
[4]

[Total: 12]

5 ***Adrenaline*** is a natural hormone and acts as a stimulant when secreted directly into the bloodstream. It has the following structure:



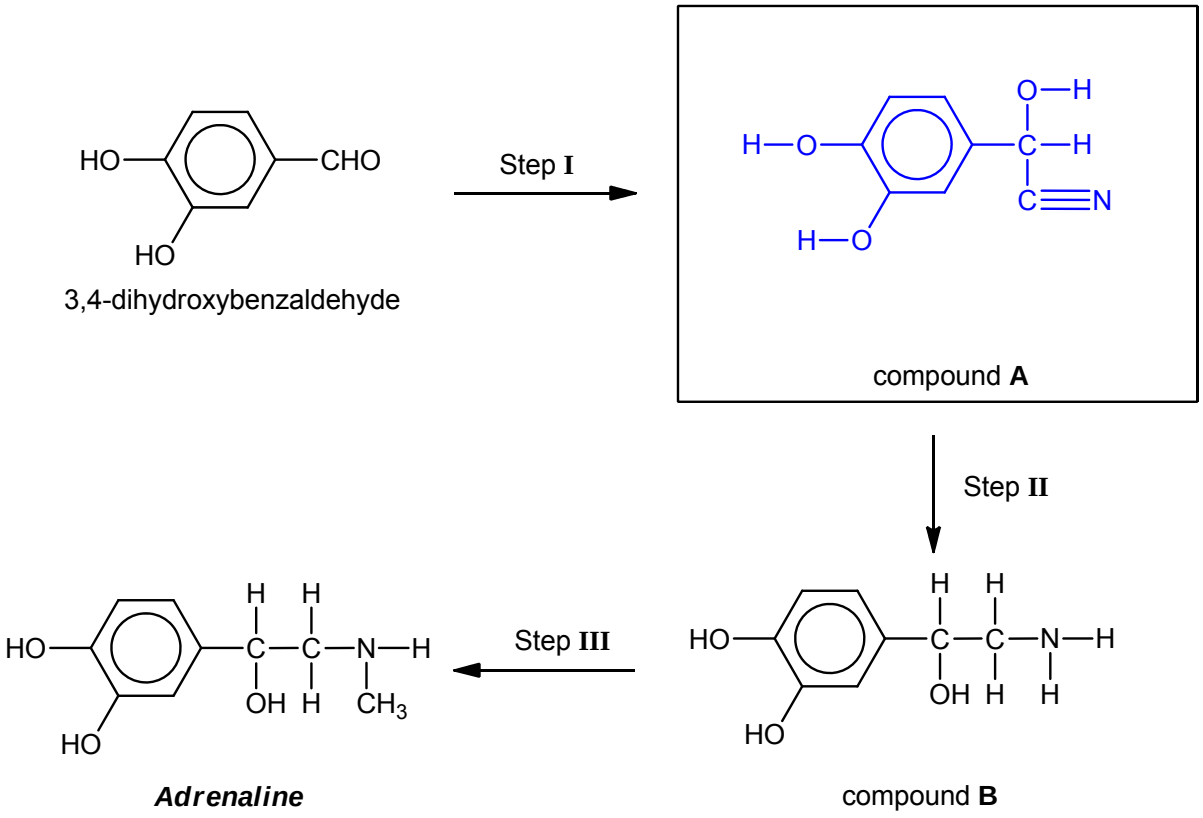
(a) In the boxes below, give the structural formulae of the organic compounds formed when ***Adrenaline*** reacts with each of the following reagents and under the stated conditions.

Reagents and conditions	Product
(i) $SOCl_2$	
(ii) CH_3COOH, r.t.p	
(iii) Na	

[4]

(b) Reactions involving the formation of a hydroxynitrile (cyanohydrin) as an intermediate are useful because of the further reactions that can be carried out. More importantly, it increases the number of carbon atoms in a chain as a C-C bond is formed.

Adrenaline can be synthesised from 3,4-dihydroxybenzaldehyde via the following reaction pathway with a hydroxynitrile being the intermediate.



(i) Draw the **displayed formula** of compound **A** in the box provided above.

(ii) State the reagents and conditions required for Steps **I** – **III** by completing the table below.

Steps	Reagents and conditions
I	HCN, trace amount of KCN or NaOH, 10-20˚C
II	H_2, Ni catalyst, heat or $LiAlH_4$ in dry ether
III	Ethanolic CH_3Br, heat

[4]

(c) The Grignard reaction is another versatile tool for forming C-C bonds. In 1900, Victor Grignard reported that a warm solution of bromoethane can react with magnesium in a dry, non-polar solvent to give an organomagnesium compound with formula of CH_3CH_2MgBr. The carbon-magnesium bond is polarised and the carbon directly bonded to magnesium is ***basic***.

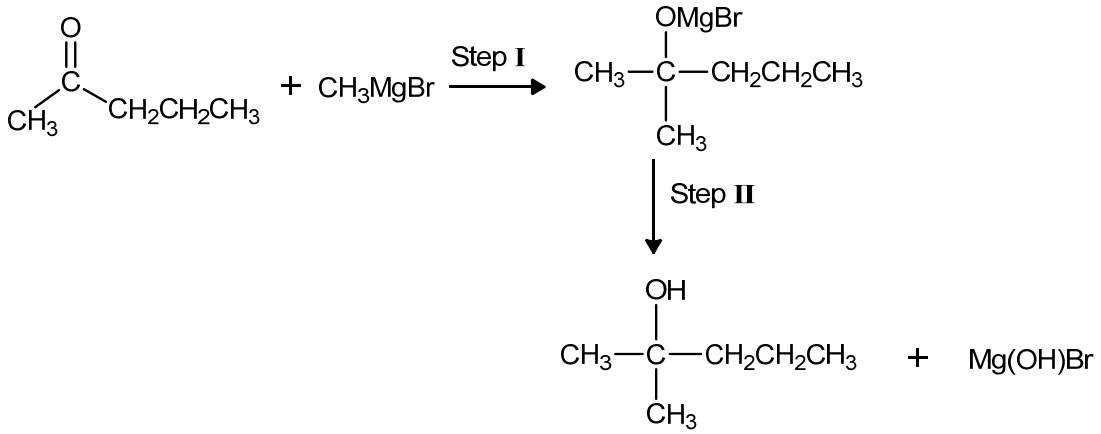
Grignard reagents, with different alkyl or aryl groups can be prepared and are widely used in organic synthesis.

$$R\text{–}X + Mg \rightarrow R\text{–}MgX$$
Grignard reagent

(where R is an alkyl or aryl group and X can be C*l*, Br or I)

The Grignard reagent formed can then react with aldehydes and ketones to yield secondary and tertiary alcohols respectively.

An example of the use of Grignard reagent is the two-step reaction of pentan-2-one with CH_3MgBr.

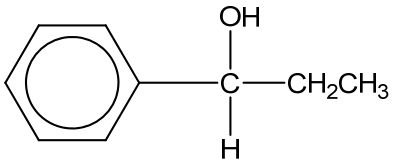


(i) Identify the types of reactions that occur in Steps I and II.

Step **I**: nucleophilic addition

Step **II**: hydrolysis

(ii) Draw the structure of the final organic compound formed when benzaldehyde reacts with CH_3CH_2MgBr.



(iii) Suggest why this method of using the Grignard reagent is **not** suitable for the preparation of ***Adrenaline*** from 3,4-dihydroxybenzaldehyde.

3,4-dihydroxybenzaldehyde contains **acidic phenolic** groups which will react with the basic Grignard reagent.

[4]

[Total: 12]