RIVER VALLEY HIGH SCHOOL
JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	18J								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **24 September 2019**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of 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.

Section B
Answer **one** question.

Begin each question on a fresh page.
A Data Booklet is provided. Do not write anything on it.
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 question.
At the end of the examination, fasten all your work securely together.

This document consists of **15** printed pages and 1 blank page.

Section A

Answer **all** the questions from this section.

1 **(a)** **(i)** Hydrogen halide, HX, is soluble in both polar and nonpolar solvents. Describe the interactions formed when HX dissolves in polar solvents such as water. **[1]**

(ii) The boiling points of the first four hydrogen halides down Group 17 are listed in the following table.

Table 1.1

Hydrogen Halide	Boiling Point / °C
HF	20
HC*l*	−85
HBr	−67
HI	−35

Describe and explain the trend. **[2]**

(iii) Four gas jars containing a hydrogen halide from Table 1.1 were prepared. When a red-hot steel needle is introduced to the gas jars respectively, two of them showed intense colour changes while the other two showed no visible change.

With reference to the *Data Booklet*, describe and explain the observations. **[3]**

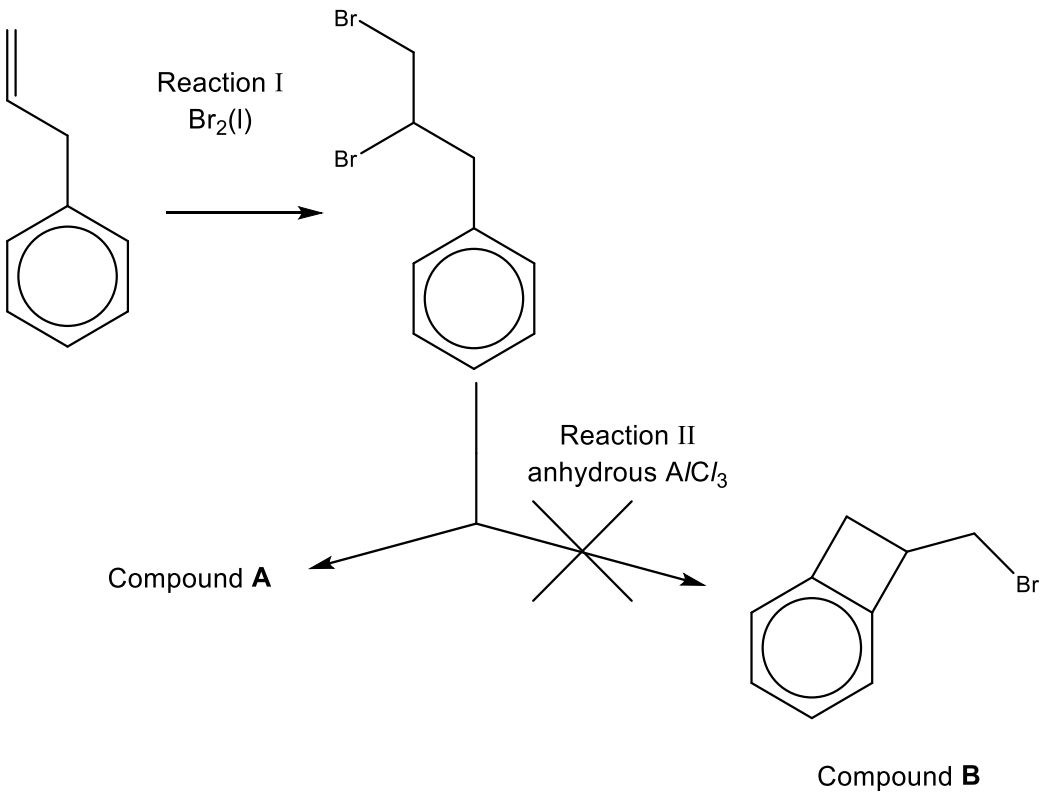
(b) **(i)** In an experiment, an excess of 5.00 g AgC*l*(s) was added to 1 dm^3 solution of 0.00100 mol dm^{-3} NaC*l* and allowed to reach equilibrium at 298 K. The mixture was then filtered and the residue was dried thoroughly. 100 cm^3 of the filtrate required the addition of 4.00×10^{-12} mol of NaBr for the first trace of AgBr to appear.

Given that solubility of AgBr in water is 0.140 mg L^{-1}, calculate the concentration of Ag^+ ions in the 100 cm^3 filtrate. **[2]**

(ii) Calculate the solubility of AgC*l* in mol dm^{-3}. **[2]**

(iii) Calculate the mass of residue collected from the filtration. **[1]**

(c)



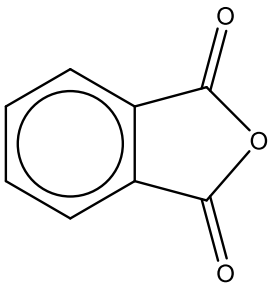
(i) There are two possible intermediates for Reaction I. Draw the structure of the more stable intermediate and explain its stability. **[2]**

(ii) Describe the mechanism of Reaction II to form Compound **A**. In your answer, use curly arrows to indicate the movement of electrons. **[2]**

(iii) With reference to the hybridisation of carbon atoms, explain why compound **B** is not a product from Reaction II. **[2]**

[Total: 17]

2 **(a)** Phthalic anhydride is the acid anhydride of phthalic acid. It is an important industrial chemical for the synthesis of phthalic esters, which are used as plasticisers to soften plastics

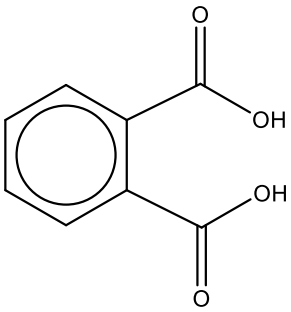


Phthalic anhydride

(i) Given that phthalic anhydride reacts with an alcohol to form a monoester as the only product, write an equation for the reaction of phthalic anhydride with propan-1-ol. **[1]**

(ii) The esterification of the monoester is more difficult to carry out and requires the removal of an inorganic by-product. Suggest the identity of the by-product. **[1]**

(b) Hydrolysis of phthalic anhydride produces phthalic acid, which is an aromatic dicarboxylic acid that can ionise in stages. Some information on phthalic acid and another aromatic acid are given below.



Phthalic acid

Table 2.1

	pK_1	pK_2
Phthalic acid	2.89	5.51
Benzoic acid	4.20	-

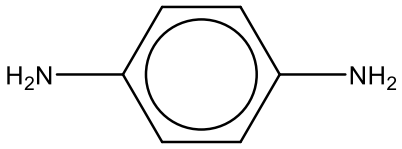
(i) Suggest a reason why the pK_2 of phthalic acid is higher than its pK_1. **[1]**

(ii) Calculate the pH of a solution that is obtained after 50 cm^3 of 0.1 mol dm^{-3} of NaOH is added to 10 cm^3 of 0.2 mol dm^{-3} phthalic acid. **[2]**

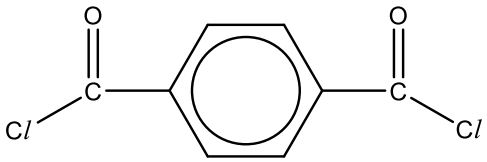
(iii) Sketch the pH-volume added curve you would expect to obtain when 50 cm^3 of 0.1 mol dm^{-3} of NaOH is added to 10 cm^3 of 0.2 mol dm^{-3} phthalic acid. Include relevant details from **(ii)** on your graph. **[3]**

(iv) Predict the structure of the ionic compound that will be formed when sodium benzoate is added to phthalic acid. **[1]**

(c) Kevlar is a heat resistant and strong synthetic polymer that is used in bullet-proof vests. Kevlar is synthesised in solution from the monomers of 1,4-phenylene-diamine and terephthaloyl chloride.



1,4-phenylene-diamine

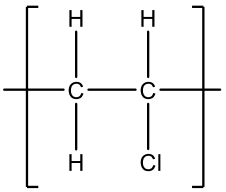


terephthaloyl chloride

(i) State the type of reaction that occurs between 1,4-phenylene-diamine and terephthaloyl chloride that will result in the formation of a polymer. **[1]**

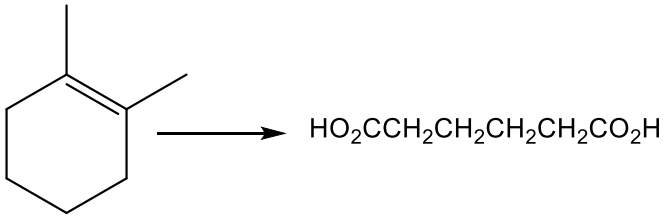
(ii) A repeating unit is a part of a polymer whose repetition would produce the complete polymer chain (except the end groups) by linking the repeating units together successively along the chain.

For example, the repeating unit of polyvinyl chloride is shown below.



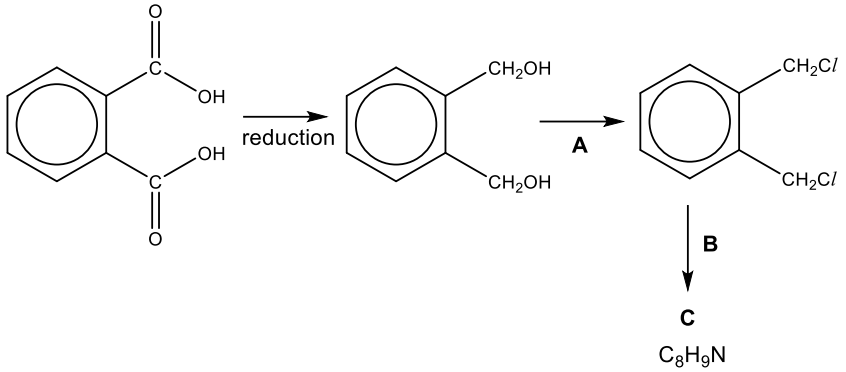
Draw the structure of the repeating unit of Kevlar. **[1]**

(d) Polyprotic organic acids are usual precursors in synthesis. Suggest how the polyprotic organic acid below can be synthesised. Indicate reagents and conditions you would use in each step, including the structure of the intermediate(s), if any.



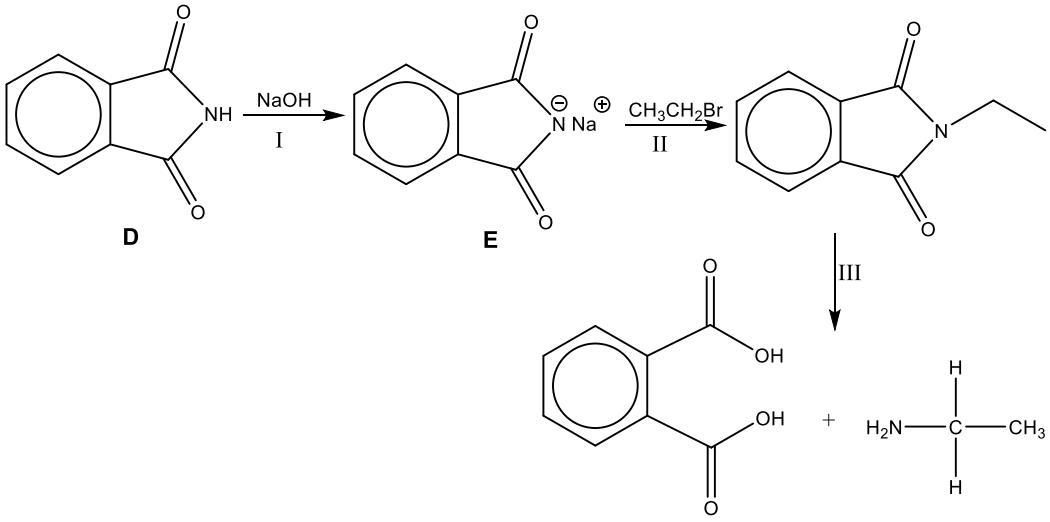
[2]

(e) Phthalic acid undergoes the reaction scheme below.



Suggest the reagents and conditions for Reactions **A** and **B** as well as the structure for Compound **C**. **[3]**

(f) Compound **D** is a useful intermediate for making primary amines from bromoalkanes, by the following method.



(i) State the types of reaction in Steps I, II and III. **[3]**

(ii) Suggest reagents and conditions for Step III. **[1]**

(iii) Draw a simple diagram to show how a water molecule can be attached to the anion in **E**. Label your diagram to show the dominant type of interaction involved. **[1]**

(iv) When **D** undergoes combustion, a student, Eugene, predicted that one of the likely products is either NO or N_2 gas. He carried out a simple experiment to determine the combustion equation for **D**.

First, he burnt 0.5 g of **D** in air. After combustion, he passed the gaseous mixture through potassium hydroxide and measured the volume of gas remaining at 30 ºC and 1 atm. Eugene determined that the gaseous volume was 42.26 cm^3.

Using the information above, determine the identity of the gas and write an equation for the combustion reaction of **D**. **[3]**

[Total: 24]

3 Iron is the second most abundant metal in the earth's crust and is abundantly used in building materials such as steel. The two most common oxidation states of iron in its compounds are +2 and +3.

(a) When 5 cm^3 of 0.2 mol dm^{-3} iron(III) chloride solution was added to 10 cm^3 of 0.6 mol dm^{-3} sodium cyanide solution, the solution turned red.

When the resultant solution undergoes a redox reaction, the solution turned yellow and the complex **Y** formed has a M_r of 211.8.

Deduce, with the help of calculations and the *Data Booklet*, the formulae of the complexes formed when the solution turned red and yellow respectively. Write equations when appropriate. **[2]**

(b) Explain the following observations regarding iron and its compounds. Support your answers with data from the *Data Booklet* where appropriate.

(i) The electrical conductivity of iron is higher than that of calcium. **[1]**

(ii) The pH of a solution of iron(III) chloride is lower than the pH of a solution of iron(II) chloride of the same concentration. **[2]**

(c) Iron(III) ions catalyse the reaction between aqueous potassium peroxodisulfate, $K_2S_2O_8$, and aqueous potassium iodide.

(i) Explain, with the help of the *Data Booklet*, the role of Fe^{3+} in the reaction. **[2]**

(ii) Draw a fully-labelled energy profile diagram to show the above reaction, which is exothermic. **[3]**

(d) Compound **V**, with the molecular formula $C_8H_9NO_2$, is found to be able to relief pain and reduce fever. At room temperature, **V** is insoluble in water and dilute acids but soluble in aqueous sodium hydroxide. **V** reacts with aqueous bromine to form **W**, $C_8H_7NO_2Br_2$.

On heating **V** with dilute hydrochloric acid, compounds **X** and **Y** are formed. **X**, with the molecular formula C_6H_8NOCl, is soluble in water.

Y, on reduction with lithium aluminium hydride, forms **Z**. **Z** reacts with alkaline aqueous iodine to form a yellow precipitate.

Identify compounds **V** to **Z** and briefly explain the reactions described. **[9]**

[Total: 19]

Section B

Answer **one** question from this section.

4. Volatile organic compounds (VOCs) are carbon-containing chemical vapours that can come from both man-made and natural sources. VOCs generally have high vapour pressures at ordinary room temperatures.

The table below shows a list of the common VOCs found around us.

Table 4.1

VOC	Formula	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J mol^{-1} K^{-1}
Benzene	C_6H_6	+33.9	+113.6
Ethanol	C_2H_5OH	+38.6	+109.7
Methylbenzene	$C_6H_5CH_3$	+38.1	+87.3
Propanone	CH_3COCH_3	+31.3	+95.0

(a) **(i)** Using the Gibbs Equation,

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap},$$

explain whether the process of vaporisation is an enthalpy-driven or entropy-driven reaction. **[2]**

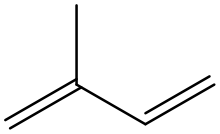
(ii) From Table 4.1, state the most volatile VOC at 330 K and calculate the corresponding ΔG_{vap}. **[1]**

(b) Dichloromethane, another common VOC of formula CH_2Cl_2, is synthesised industrially from methane via free radical chlorination.

(i) State the reagent and condition required to synthesise dichloromethane from methane. **[1]**

(ii) Describe the mechanism involved in this synthesis, showing the steps that produce dichloromethane. **[3]**

(c) Isoprene, C_5H_8, is one of the biologically generated VOCs by plants and algae. It is used to manufacture synthetic rubbers and elastomer plastics. It appears as a colourless, volatile liquid and is known to cause respiratory irritation from overexposure to its vapour.



(i) State the IUPAC nomenclature of isoprene. **[1]**

(ii) Yet, isoprene is the most abundant hydrocarbon measurable in human breath.

The estimated production rate of isoprene in the human body is 0.15 μmol kg^{-1} h^{-1}.

Calculate the mass, in mg, of isoprene estimated to be produced by a 65 kg person in a day.

[1 μmol = 10^{-6} mol] **[1]**

A gaseous mixture, made up of isoprene (C_5H_8) and carbon disulfide (CS_2), is prepared in a corresponding volume ratio of 1 : n.

The mixture is completely combusted with an excess of oxygen at 25 ^oC and 1 atm. After combustion, there was an overall volume contraction of 70 cm^3.

The resultant product mixture contains three gases, two of which are acidic, and water. Upon passing this mixture through aqueous sodium hydroxide, a further contraction of 170 cm^3 took place.

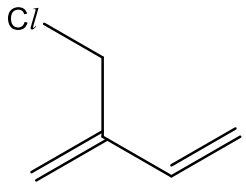
(iii) Given that complete combustion of carbon disulfide produces carbon dioxide and sulfur dioxide, write balanced equations for the complete combustion of isoprene and of carbon disulfide separately. **[2]**

(iv) Assuming that the volume of isoprene is x cm^3 in the gaseous mixture, find n using the balanced equations in **(c)(iii)**.

You may find proving the following expressions useful:

- $(n + 3)x = 70$ from the 1st contraction
- $(3n + 5)x = 170$ from the 2nd contraction **[3]**

(d) Compound **M**, a chlorinated form of isoprene of molecular formula C_5H_7Cl, is a liquid at room temperature.



Compound **M**

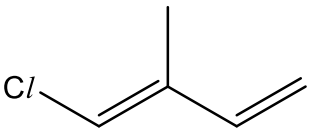
(i)

Enthalpy change of atomisation of carbon / kJ mol^{-1}	+715
Enthalpy change of vaporisation of compound **M** / kJ mol^{-1}	+30

Using the given data above and relevant data from the *Data Booklet*, construct a fully-labelled energy level diagram to calculate the enthalpy change of formation of compound **M**. **[4]**

(ii) Compound **N** is an isomer of compound **M**.

It is a liquid at room temperature and its enthalpy change of vaporisation is +30 kJ mol^{-1} as well.



Compound **N**

State the isomeric relationship between compounds **M** and **N**. **[1]**

(iii) It is found that the magnitude of its enthalpy change of formation is smaller than that of compound **M**. Suggest a possible reason for this. **[1]**

[Total: 20]

5 This question is about the chemistry of Period 3 elements.

(a) Describe the action of water on the oxides of magnesium, silicon and phosphorus.

Write equations for any reactions that occur, and suggest the pH for each of the resulting solutions.

[5]

(b) All wines contain sulfur dioxide for its anti-oxidant and anti-bacterial properties. However, if too much sulfur dioxide and sulfites are present, they would induce an unpleasant taste. Sulfur dioxide also contributes significantly to hangover.

The World Health Organisation recommends a maximum daily intake of 0.7 mg of SO_2 per kilogram of bodyweight.

Wineries use the Ripper titration to determine the concentration of SO_2 in mg L^{-1} in their wines. In a Ripper titration, 2 cm^3 of starch solution is added to 50 cm^3 of the wine in a conical flask. The wine is then titrated against a standard iodine solution.

17.70 cm^3 of 0.0100 mol dm^{-3} aqueous iodine is added until a dark colour appears and persists for at least 15 seconds.

(i) Write the balanced equation for the reaction between SO_2 and iodine. **[1]**

(ii) Determine the concentration of sulfur dioxide in the wine and state if it is advisable for a person of 70 kg to consume 400 mL of this bottle of wine. **[2]**

(c) Organometallic compounds, which contain a carbon-metal bond, are key intermediates in organic reactions to form a C–C bond. In general, when organometallic compounds are used on carbonyl compounds, alcohols are produced as shown in Fig 5.1.

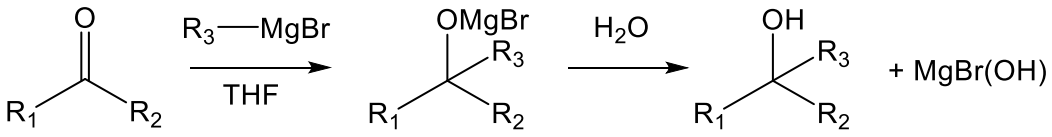


Fig 5.1

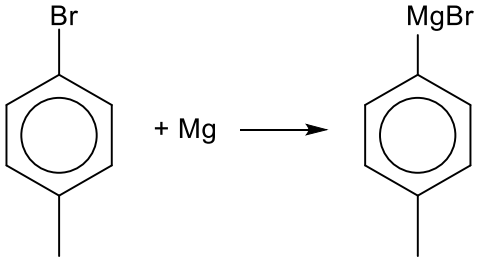
Common organometallic compounds are organolithium (contain carbon-lithium bond) and Grignard reagents (contain carbon-magnesium bond).

(i) In organolithium and Grignard reagents, carbon is a powerful nucleophile, which allows the formation of a C–C bond.

Explain how the nucleophilicity of carbon arises. **[1]**

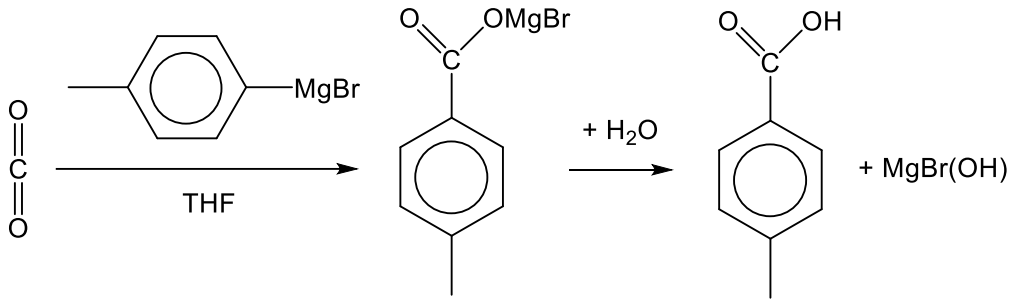
An experiment was conducted to synthesise 4-toluic acid from 4-bromotoluene using a Grignard reagent. The Grignard reagent is first synthesised by a reaction between 4-bromotoluene and magnesium. The Grignard reagent is then used on dry ice to form 4-toluic acid in tetrahydrofuran (THF) solvent.

Synthesis of Grignard reagent:



Grignard reagent

Reaction:



4-toluic acid

Fig 5.2 shows the reflux set-up of a Grignard reaction.

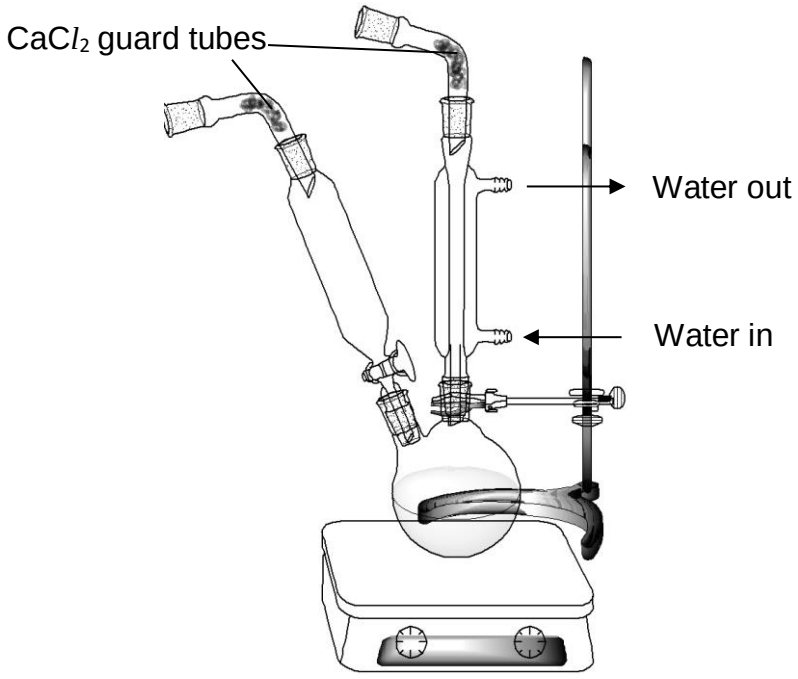


Fig 5.2

(ii) State the purpose of the calcium chloride guard tubes. **[1]**

(iii) Grignard reagents are destroyed readily upon the exposure to a small amount of moisture.

State the name of the reaction and draw the mechanism for this reaction using the Grignard reagent in Fig 5.2. **[2]**

A basic solvent extraction is used to purify the crude 4-toluic acid product. The crude product was dissolved in 20 cm^3 of dichloromethane (CH_2Cl_2) with 20 cm^3 of 10% NaOH.

The aqueous layer was extracted and combined before immersing in an ice-water bath. Concentrated hydrochloric acid was then added from a dispenser to the aqueous layer.

(iv) Explain the need for an ice-water bath in this step. **[1]**

In organic experiments, Thin Layer Chromatography (TLC) is often used to monitor the progress of a reaction and assess if the reaction is complete.

Fig. 5.3 shows a typical chromatography paper made up of silica (SiO_2) with the presence of hydroxyl groups on their surface.

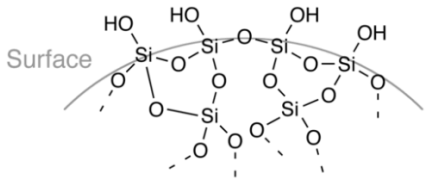


Fig. 5.3

When the reaction has proceeded for 60 minutes, a small portion of the reaction mixture, containing 4-bromotoluene and 4-toluic acid, was loaded on the TLC plate as shown in Fig. 5.4.

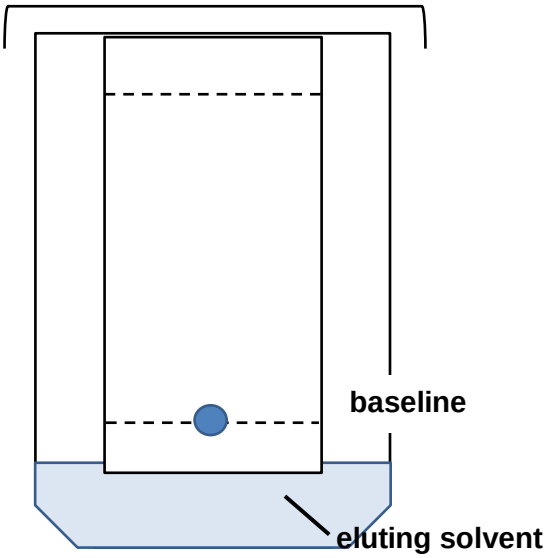


Fig. 5.4 TLC plate placed in TLC developing chamber

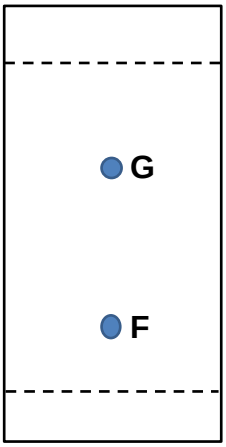


Fig. 5.5 TLC plate developed

The TLC plate was placed in a TLC developing chamber which contains an eluting solvent made up of ethyl acetate and hexane in a 1:2 volume ratio. As the eluting solvent passed through the spots on the baseline, depending on the interactions with the chromatogram and eluting solvent, the solute molecules travelled at different rates up the chromatogram. Each compound has a different retention factor, R_f, in the eluting solvent.

(v) The TLC plate is developed and the result is shown in Fig. 5.5.

Determine the R_f value of **F** in this TLC, given that the R_f is calculated as:

$$R_f = \frac{distance\ moved\ by\ solute}{migration\ distance\ moved\ by\ solvent}$$

[1]

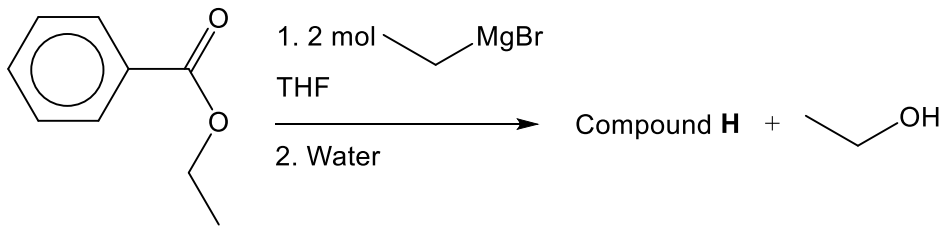
(vi) Consider the interactions between silica and 4-toluic acid, and between silica and 4-bromotoluene, identify **F** and **G**. Hence, explain the difference in the migration distance between 4-toluic acid and 4-bromotoluene.

[2]

(vii) Suggest how the R_f value of 4-toluic acid will change when the eluting solvent is changed to ethyl acetate : hexane in a 2:1 volume ratio.

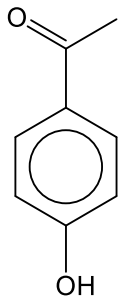
[1]

(viii)

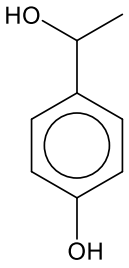


Suggest the structure for compound **H**. **[1]**

(ix) Compounds **J** and **K** are isomers of 4-toluic acid. Describe a simple chemical test to distinguish between compounds **J** and **K**.



Compound **J**



Compound **K**

[2]

[Total: 20]

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