Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
2 Write your answers on the separate writing papers provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Start each question on a fresh sheet of paper.
[Marks will be deducted if you fail to do so.]
6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions

Section B

9 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.
You are advised to show all workings in calculations.
You are reminded of the need for good English and clear presentation in your answers.

[Turn over

Section A

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

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow[CH_3OH]{Na} CH_3OCH_3 + HCl$$

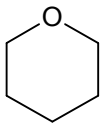
(a) **(i)** State the purpose of sodium used in the Williamson ether synthesis.

[1]

(ii) Hence, name the mechanism of the reaction.

[1]

(iii) Suggest suitable reagent(s) to synthesise each of the following ethers.

- $CH_3CH_2OCH_2CH_3$
- 

[2]

(b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $CH_3CH_2OC(CH_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	CH_3CH_2Br and $(CH_3)_3COH$
B	$(CH_3)_3CBr$ and CH_3CH_2OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning.

[2]

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	**Unit**	**DME**	**Diesel Fuel**
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m^{-3}	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg^{-1}	467.1	300
Energy released at burning	MJ kg^{-1}	27.6	42.5

**Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.*

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

(d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al_2O_3 catalyst.

(i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

(ii) State the type of catalysis that Cu-Zn/Al_2O_3 performs and explain briefly how it promotes the synthesis of DME.

[3]

(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \quad \Delta H = -13.1 \text{ kJ mol}^{-1}$$

$$2CH_3OH(l) \rightarrow CH_3OCH_3(l) + H_2O(l) \quad \Delta H = -459.1 \text{ kJ mol}^{-1}$$

Using the thermochemical equations given and any relevant data in part **(c)**, draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]

(e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.

(i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

[1]

(ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.

[3]

(iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4×10^{-4}, determine the concentration of dimethylamine hydrochloride in the solution.

[3]

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.

[1]

[Total: 25]

2 (a) Carbon undergoes combustion in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4.

[2]

(ii) ZnC_2O_4 undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

[1]

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce^{4+}/Ce^{3+} half–cell, using relevant data from the *Data Booklet*.

[1]

(ii) Using relevant data from the *Data Booklet*, deduce if the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

[1]

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is $LaNi_5H_6$ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce $LaNi_5$(s) and $Ni(OH)_2$(s), and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in **(c)(i)**, write the overall equation for the reaction that occurs during recharging.

[1]

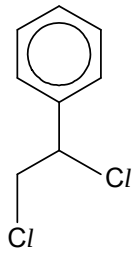
(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

[Total: 12]

3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound **Y**

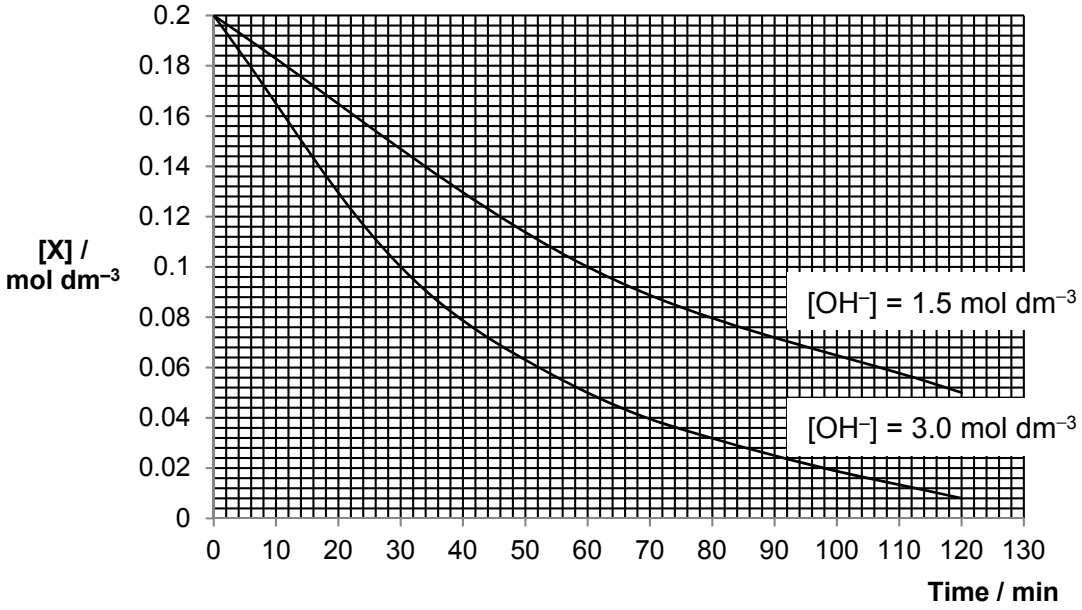
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding $AgNO_3$	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

(i) Deduce the rate equation based on the information given in Experiment **I**.

[3]

(ii) Using your answer in **(a)(i)** and the information given in Experiment **II**, deduce, with reasoning, a possible structure of **X**.

[2]

(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

(b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH^-	
		1° RX in S_N2	3° RX in S_N1
CH_3OH	Protic	1	4
H_2O	Protic	7	150 000
CH_3COOH	Protic	1	1
CH_3COCH_3	Aprotic	5000	–

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

(ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions.

[2]

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction.

[2]

(iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid?

[1]

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / mol^2 dm^{-6}
AgC*l*	1.4×10^{-5}	2.0×10^{-10}
AgBr	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide.

[1]

(ii) From the data above, calculate a value for K_{sp} of silver iodide.

[1]

(iii) Using your answer in **(c)(ii)**, calculate the solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$.

[2]

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

(v) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following equation.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

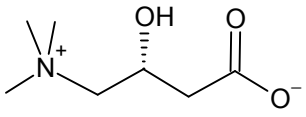
[2]

[Total: 23]

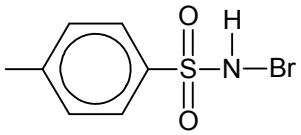
Section B

Answer **one** question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



levocarnitine



bromamine-T

(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of $RuCl_3$, was carried out in aqueous hydrochloric acid.

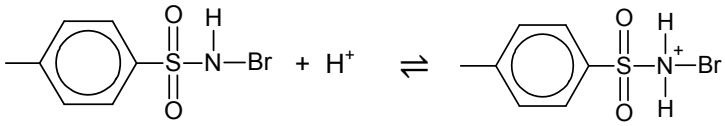
The following equilibrium exists for $RuCl_3$ in aqueous hydrochloric acid.

$$[RuCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [RuCl_6]^{3-} + H_2O$$

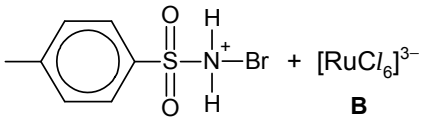
Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

[1]

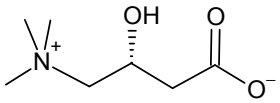
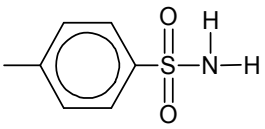
(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



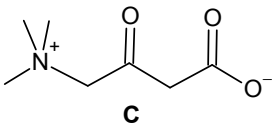
bromamine-T **A** step 1



B complex X step 2

complex X +  complex X' +  step 3

levocarnitine

complex X' →  + $[RuCl_6]^{3-}$ + HBr step 4

C

(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number.

[2]

(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, *k'*, for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a, and the pre-exponential factor, A, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.
T is the reaction temperature in Kelvin.
k' is the observed rate constant at a chosen temperature.

(i) Calculate the values of ln k' and $\frac{1}{T}$ for each of the experiments above.

[2]

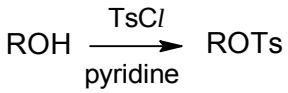
(ii) Hence plot a graph of ln k' against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

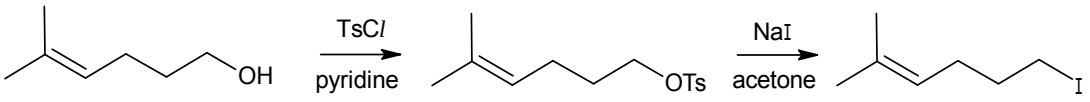
(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]

(d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

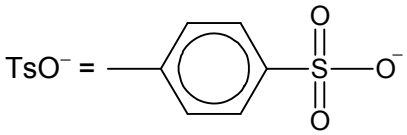


This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO^- ion formed compared to OH^-.

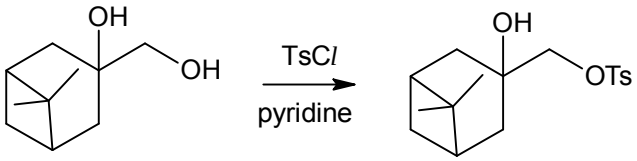
Suggest an explanation for the stability of the TsO^- ion.

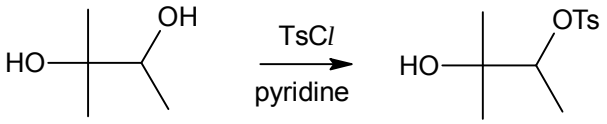


[1]

(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

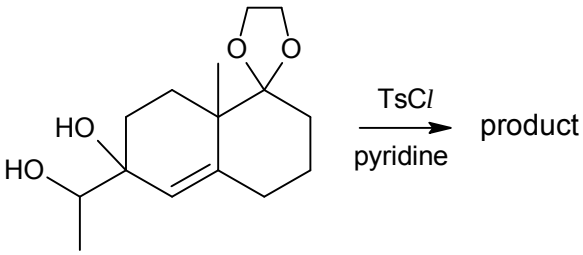
Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.





[2]

(iii) Predict the product of the following conversion.



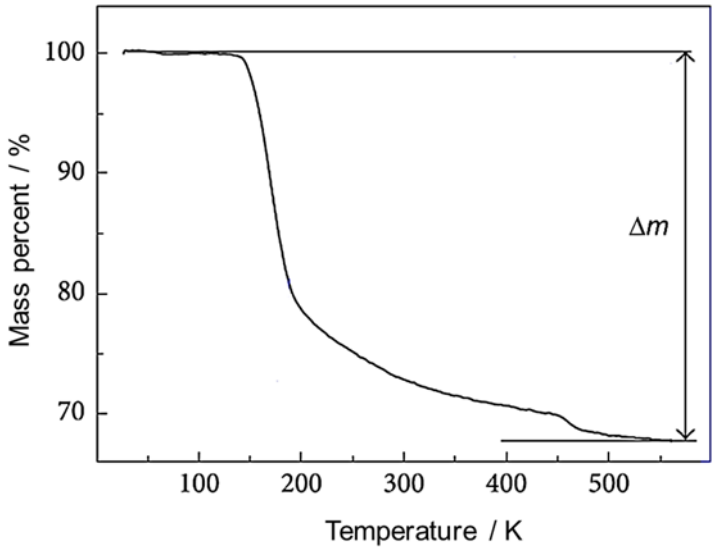
The  ring remains unaltered in the reaction.

[1]

[Total: 20]

5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $LiB_5O_8.5H_2O$ observed in the graph.

[M_r ($LiB_5O_8.5H_2O$) = 278.9]

[2]

(b) The sample of $LiB_5O_8.5H_2O$ used in **(a)** was synthesised as a system of Li_2O, B_2O_3 and H_2O in the laboratory.

(i) Deduce the molar ratio of Li_2O : B_2O_3 : H_2O in a pure sample of $LiB_5O_8.5H_2O$.

[1]

(ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2.

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ.

[2]

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is -18.2 kJ mol^{-1}.

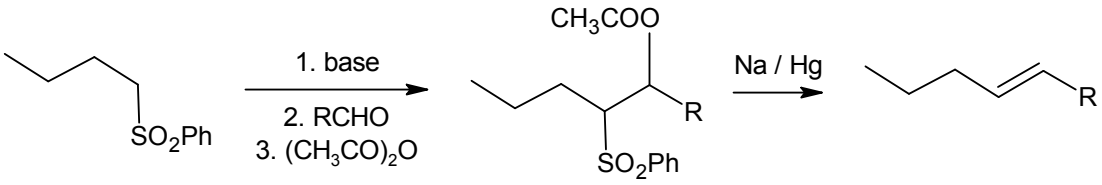
[2]

(iv) Calculate the pH of the resulting solution formed in **(c)(iii)** given that the K_b of carbonate ion is 1.995×10^{-4} mol dm^{-3}.

[3]

(d) Phenylsulfonyl ($PhSO_2$) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

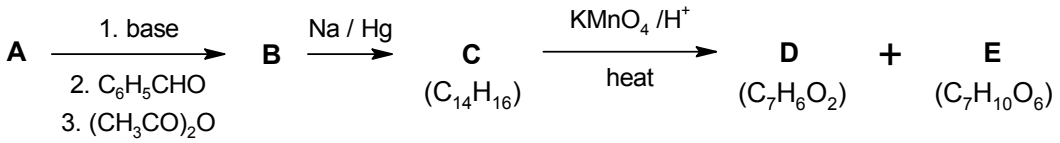
An example of Julia olefination is as follows.



(i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

Consider the reaction scheme below involving Julia olefination.



(ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**.

[1]

(iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride ($SOCl_2$) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

(iv) Hence suggest the structures of compounds **A** to **C**.

[3]

[Total: 20]