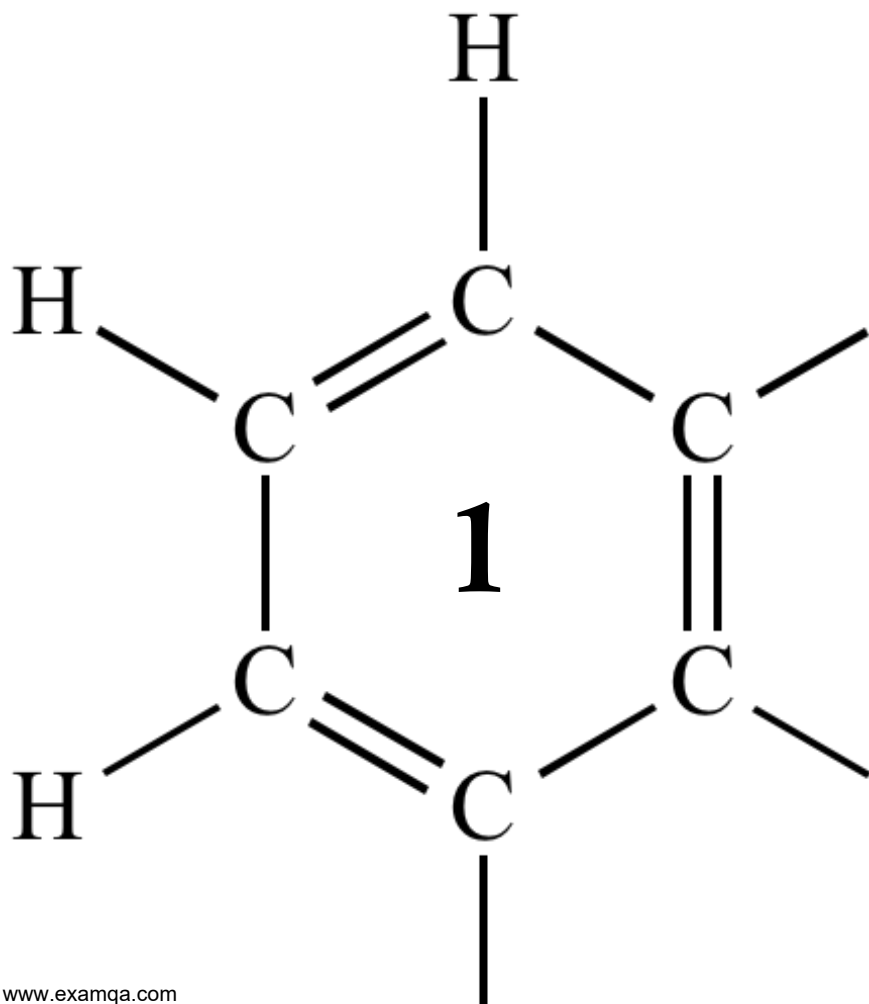


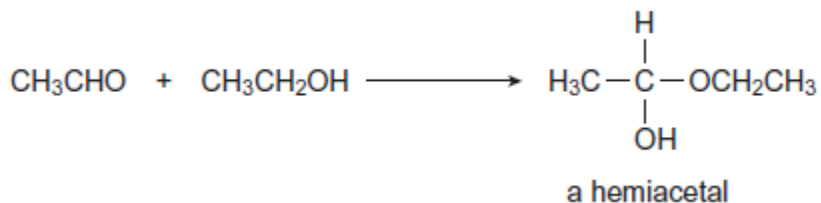
AQA A2 CHEMISTRY  
**ISOMERISM ~ CARBONYLS**

OPTICAL ISOMERS



1

Hemiacetals and acetals are compounds formed by the reaction of aldehydes with alcohols, such as the reaction of ethanal with ethanol.



- (a) (i) Use your knowledge of carbonyl mechanisms to suggest the name of the mechanism of this reaction.

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(1)

- (ii) Outline how an ethanol molecule reacts with an ethanal molecule in the first step of this mechanism. Include two curly arrows to show the movement of electron pairs.

(2)

- (b) The reaction produces a racemic mixture of chiral molecules.

- (i) Explain the meaning of the term racemic mixture.

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(1)

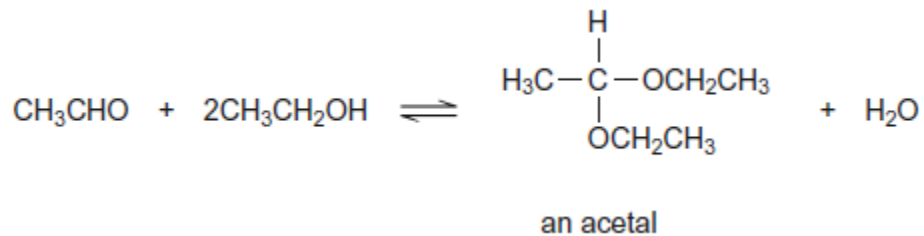
- (ii) State the relationship between two chiral molecules with the same structural formula.

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(1)

- (c) In the presence of an acid catalyst such as dry hydrogen chloride, ethanal reacts with an excess of ethanol to form an acetal.

The overall reaction of ethanal with an excess of ethanol forms an equilibrium mixture as shown. All reactants and products are liquids.



A mixture of 0.75 mol of ethanal and 5.00 mol of ethanol was left to reach equilibrium in the presence of dry hydrogen chloride at a given temperature. The equilibrium mixture contained 0.42 mol of the acetal.

- (i) Calculate the amount, in moles, of ethanal and of ethanol in this equilibrium mixture.

Amount of ethanal ..... mol

Amount of ethanol ..... mol

Space for working .....

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(2)

- (ii) In a different experiment using the same reaction as in part (c), an equilibrium mixture was established at a given temperature. This mixture contained 0.58 mol of ethanal, 3.76 mol of ethanol, 0.37 mol of the acetal and 0.65 mol of water in a total volume of 310 cm<sup>3</sup>.

Write an expression for the equilibrium constant  $K_C$  for this reaction.

Calculate a value for  $K_C$  at this temperature. Give units with your answer.

$K_C$ .....

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Calculation .....

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(4)

- (d) Draw the structure of the acetal (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) formed by the reaction of ethanal with ethane-1,2-diol.

(1)

(Total 12 marks)

2

Butanone is reduced in a two-step reaction using NaBH<sub>4</sub> followed by dilute hydrochloric acid.

- (a) Write an overall equation for the reduction of butanone using [H] to represent the reductant.

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(1)

- (b) By considering the mechanism of the reaction, explain why the product has **no** effect on plane polarised light.

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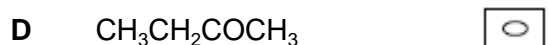
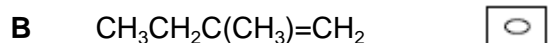
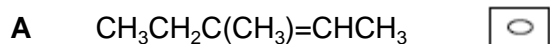
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(6)  
(Total 7 marks)

3

Which compound forms optically active compounds on reduction?



(Total 1 mark)

4

The carbonyl compound  $\text{CH}_3\text{CH}_2\text{CHO}$  reacts very slowly with HCN

- (a) Name and outline a mechanism for the reaction of  $\text{CH}_3\text{CH}_2\text{CHO}$  with HCN

Name of mechanism .....

Mechanism

(5)

(b) The reaction in part (a) produces a pair of enantiomers.

(i) Draw the structure of each enantiomer to show how they are related to each other.

(2)

(ii) State and explain how you could distinguish between the two enantiomers.

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(2)

(c) Give the IUPAC name of the product of the reaction in part (a).

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(1)

(d) In practice, KCN rather than HCN is added to the carbonyl compound.

Given that  $K_a$  for HCN =  $4.0 \times 10^{-10} \text{ mol dm}^{-3}$ , suggest why the reaction with HCN is very slow.

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(2)

- (e) Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.



- (i) Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

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(1)

- (ii) The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

(1)

- (iii) Name the type of polymerisation involved in part (ii)

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(1)

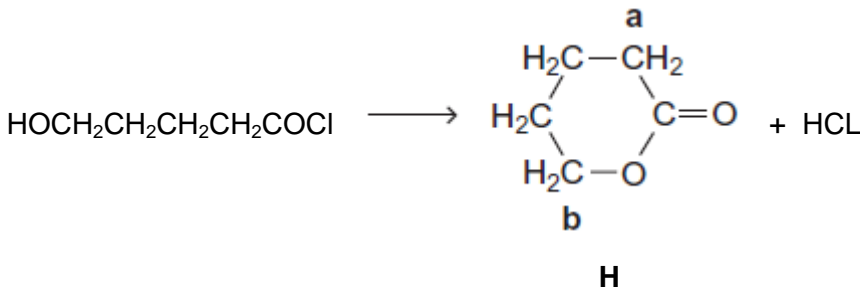
(Total 15 marks)

5

This question is about some isomers of  $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



(i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the  $^{13}C$  n.m.r.  $\delta$  value for the carbon atom labelled **a** and the  $\delta$  value for the carbon atom labelled **b**.

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(7)



- (ii)  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$  can also react to form a polyester in a mechanism similar to that in part (i).

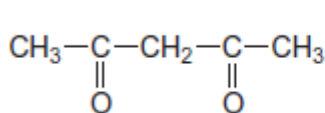
Draw the repeating unit of the polyester and name the type of polymerisation involved.

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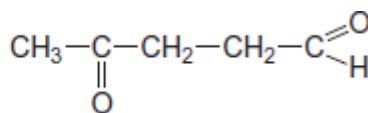
(2)

- (b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the  $^1\text{H}$  n.m.r. spectrum of each compound.



**J**



**K**

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(5)

- (c) Draw the structure of each of the following isomers of  $C_5H_8O_2$   
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

**L** is methyl 2-methylpropenoate.

**M** is an ester that shows E-Z stereoisomerism.

**N** is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

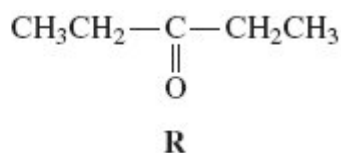
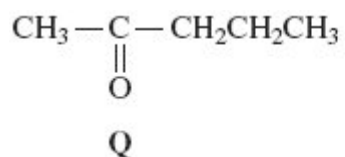
**P** is an optically active carboxylic acid.

**Q** is a cyclic compound that contains a ketone group and has only two peaks in its  $^1H$  n.m.r. spectrum.

(5)  
(Total 19 marks)

6

Two isomeric ketones are shown below.



- (a) Name and outline a mechanism for the reaction of compound **Q** with HCN and name the product formed.

Name of mechanism .....

Mechanism

Name of product .....

(6)

- (b) Some students were asked to suggest methods to distinguish between isomers **Q** and **R**.

One student suggested testing the optical activity of the products formed when **Q** and **R** were reacted separately with HCN.

By considering the optical activity of these products formed from **Q** and **R**, explain why this method would **not** distinguish between **Q** and **R**.

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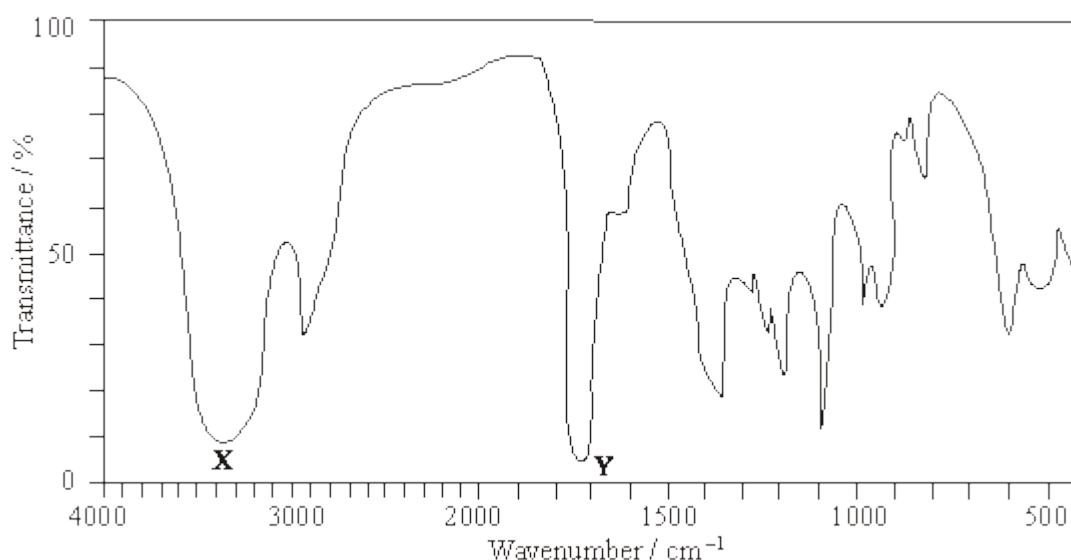
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(3)  
(Total 9 marks)

7

- (a) The infra-red spectrum of compound **A**,  $C_3H_6O_2$ , is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

(6)

(b) Draw the structures of the three **branched-chain** alkenes with molecular formula  $C_5H_{10}$

Draw the structures of the three dibromoalkanes,  $C_5H_{10}Br_2$ , formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

(10)  
(Total 16 marks)

8

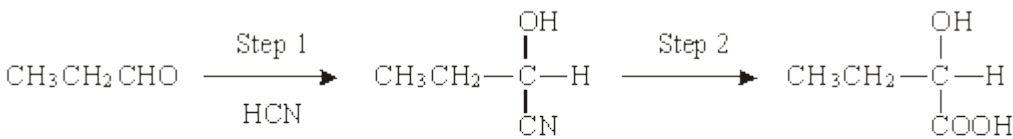
Which one of the following can exhibit both geometrical and optical isomerism?

- A  $(CH_3)_2C=CHCH(CH_3)CH_2CH_3$
- B  $CH_3CH_2CH=CHCH(CH_3)CH_2CH_3$
- C  $(CH_3)_2C=C(CH_2CH_3)_2$
- D  $CH_3CH_2CH(CH_3)CH(CH_3)C=CH_2$

(Total 1 mark)

9

Consider the reaction sequence shown below.



propanal

Q

(a) Name and outline a mechanism for the reaction in Step 1.

Name of mechanism .....

Mechanism

(5)

- (b) (i) Name compound **Q** formed in Step 2.

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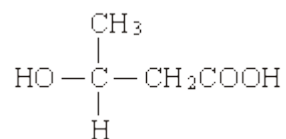
- (ii) Two stereoisomers are formed by the dehydration of **Q**. Give the structures of these two isomers and name the type of stereoisomerism shown.

*Structures of isomers*

*Type of stereoisomerism* .....

**(4)**

- (c) An isomer of **Q** which has the structure shown below is polymerised to form the biodegradable polymer known as PHB.



- (i) Draw the repeating unit of the polymer PHB.

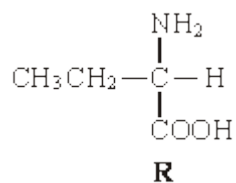
- (ii) Suggest a reason why the polymer is biodegradable.

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**(2)**

(d) The amino acid **R** is shown below.



- (i) Draw the structure of the zwitterion formed by **R**.
- (ii) Draw the structure of the major organic product formed when an excess of **R** is reacted with bromomethane.
- (iii) Name the mechanism of the reaction which results in the formation of the product given in part (ii).

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**(3)**  
**(Total 14 marks)**