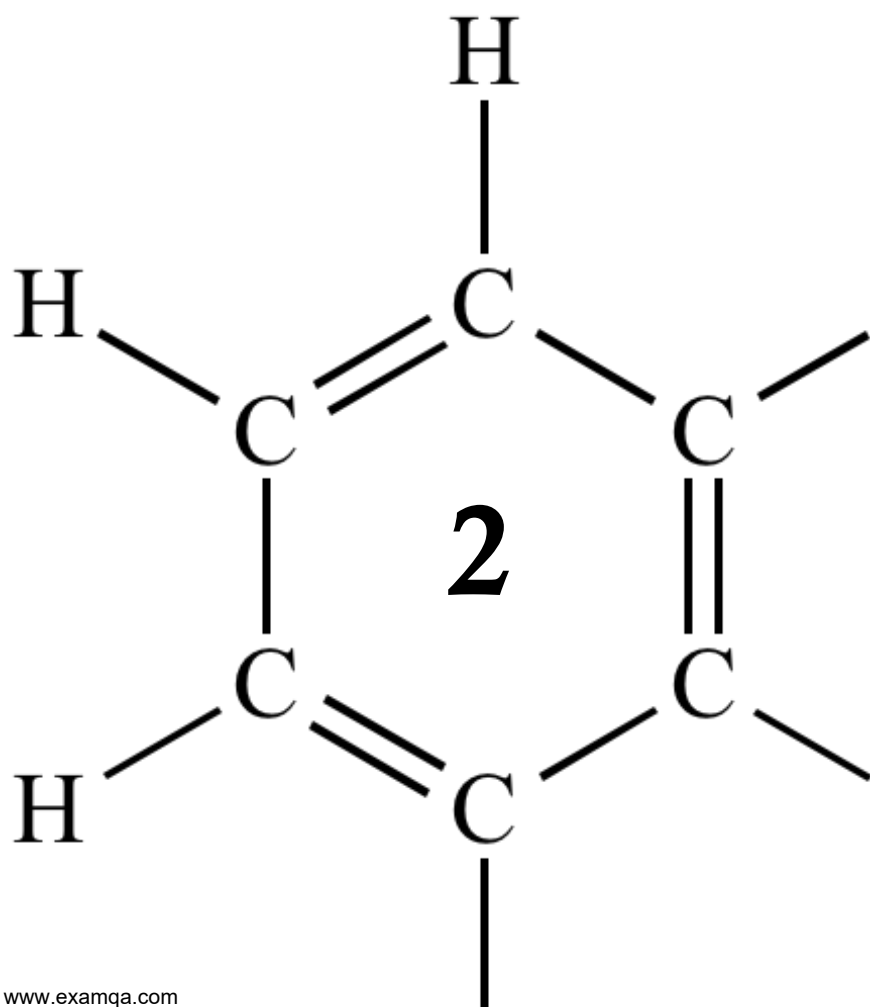


AQA A2 CHEMISTRY

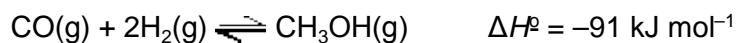
# ISOMERISM ~ CARBONYLS

CARBOXYLIC ACIDS + ESTERS



1

Synthesis gas is a mixture of carbon monoxide and hydrogen. Methanol can be manufactured from synthesis gas in a reversible reaction as shown by the following equation.



- (a) A sample of synthesis gas containing 0.240 mol of carbon monoxide and 0.380 mol of hydrogen was sealed together with a catalyst in a container of volume 1.50 dm<sup>3</sup>. When equilibrium was established at temperature T<sub>1</sub> the equilibrium mixture contained 0.170 mol of carbon monoxide.

Calculate the amount, in moles, of methanol and the amount, in moles, of hydrogen in the equilibrium mixture.

Methanol .....

Hydrogen .....

(2)

- (b) A different sample of synthesis gas was allowed to reach equilibrium in a similar container of volume 1.50 dm<sup>3</sup> at temperature T<sub>1</sub>

At equilibrium, the mixture contained 0.210 mol of carbon monoxide, 0.275 mol of hydrogen and 0.0820 mol of methanol.

- (i) Write an expression for the equilibrium constant K<sub>c</sub> for this reaction.

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.....

(1)

- (ii) Calculate a value for K<sub>c</sub> for the reaction at temperature T<sub>1</sub> and state its units.

Calculation .....

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Units .....

.....

(4)

- (iii) State the effect, if any, on the value of K<sub>c</sub> of adding more hydrogen to the equilibrium mixture.

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(1)

- (c) The temperature of the mixture in part (b) was changed to  $T_2$  and the mixture was left to reach a new equilibrium position. At this new temperature the equilibrium concentration of methanol had increased.

Deduce which of  $T_1$  or  $T_2$  is the higher temperature and explain your answer.

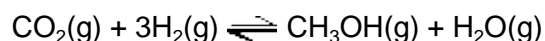
Higher temperature .....

Explanation .....

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(3)

- (d) The following reaction has been suggested as an alternative method for the production of methanol.



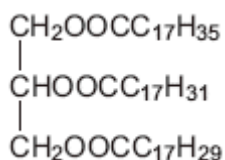
The hydrogen used in this method is obtained from the electrolysis of water.

Suggest **one** possible environmental disadvantage of the production of hydrogen by electrolysis.

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(1)

- (e) One industrial use of methanol is in the production of biodiesel from vegetable oils such as



Give the formula of **one** compound in biodiesel that is formed by the reaction of methanol with the vegetable oil shown above.

.....

(1)

(Total 13 marks)

**2**

Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

(a) Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

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**(4)**

(b) Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

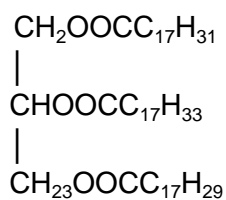
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**(3)**

(c) Name and outline a mechanism for the reaction of  $\text{CH}_3\text{COCl}$  with  $\text{CH}_3\text{OH}$  to form an ester.

(5)

(d) The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.



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(3)

- (e) Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

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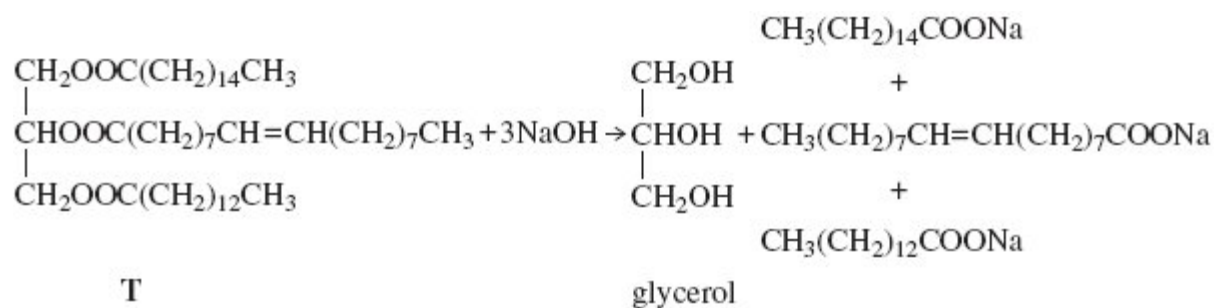
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(4)  
(Total 19 marks)

3

The triester, **T**, shown below is found in palm oil. When **T** is heated with an excess of sodium hydroxide solution, the alcohol glycerol is formed together with a mixture of three other products as shown in the following equation.



- (a) (i) Give the IUPAC name for glycerol.

.....

(1)

- (ii) Give a use for the mixture of sodium salts formed in this reaction.

.....

(1)

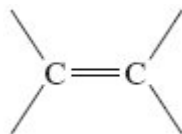
(b) When **T** is heated with an excess of methanol, glycerol is formed together with a mixture of methyl esters.

(i) Give a use for this mixture of methyl esters.

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(1)

(ii) One of the methyl esters in the mixture has the IUPAC name methyl (*Z*)-octadec-9-enoate. Draw **two** hydrogen atoms on the diagram below to illustrate the meaning of the letter *Z* in the name of this ester.



(1)

(iii) One of the other methyl esters in the mixture has the formula  $\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3$ . Write an equation for the complete combustion of one molecule of this ester.

.....

(1)

(Total 5 marks)

4

(a) Write an equation for the formation of methyl propanoate,  $\text{CH}_3\text{CH}_2\text{COOCH}_3$ , from methanol and propanoic acid.

.....

(1)

- (b) Name and outline a mechanism for the reaction between methanol and propanoyl chloride to form methyl propanoate.

*Name of mechanism* .....

*Mechanism*

(5)

- (c) Propanoic anhydride could be used instead of propanoyl chloride in the preparation of methyl propanoate from methanol. Draw the structure of propanoic anhydride.

(1)

- (d) (i) Give **one** advantage of the use of propanoyl chloride instead of propanoic acid in the laboratory preparation of methyl propanoate from methanol.

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- (ii) Give **one** advantage of the use of propanoic anhydride instead of propanoyl chloride in the industrial manufacture of methyl propanoate from methanol.

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(2)



(e) An ester contains a benzene ring. The mass spectrum of this ester shows a molecular ion peak at  $m/z = 136$ .

(i) Deduce the molecular formula of this ester.

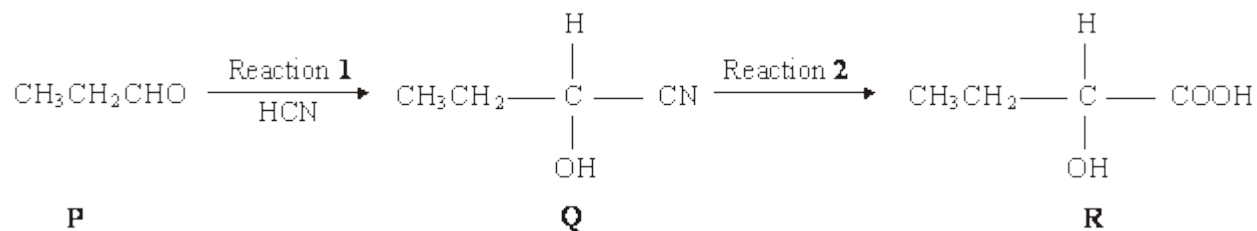
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(ii) Draw **two** possible structures for this ester.

(3)  
(Total 12 marks)

5

Consider the sequence of reactions below.



(a) Name and outline a mechanism for Reaction 1.

Name of mechanism .....

Mechanism

(5)

(b) (i) Name compound **Q**

.....

(ii) The molecular formula of **Q** is  $C_4H_7NO$ . Draw the structure of the isomer of **Q** which shows geometrical isomerism and is formed by the reaction of ammonia with an acyl chloride.

**(3)**

(c) Draw the structure of the main organic product formed in each case when **R** reacts separately with the following substances:

(i) methanol in the presence of a few drops of concentrated sulphuric acid;

(ii) acidified potassium dichromate(VI);

(iii) concentrated sulphuric acid in an elimination reaction.

**(3)**  
**(Total 11 marks)**

6

(a) Compound **A**,  $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$ , is an ester. Name this ester and write an equation for its reaction with aqueous sodium hydroxide.

Name .....

Equation .....

(2)

(b) The initial rate of reaction between ester **A** and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm <sup>-3</sup>	Initial concentration of <b>A</b> / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.040	0.030	$4.0 \times 10^{-4}$
2	0.040	0.045	$6.0 \times 10^{-4}$
3	0.060	0.045	$9.0 \times 10^{-4}$
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

Order with respect to **A** .....

Order with respect to NaOH .....

Initial rate in Experiment 4 .....

.....

(3)

(c) In a further experiment at a different temperature, the initial rate of reaction was found to be  $9.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$  when the initial concentration of **A** was  $0.020 \text{ mol dm}^{-3}$  and the initial concentration of NaOH was  $2.00 \text{ mol dm}^{-3}$ .

Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

(i) Write a rate equation for the reaction under these new conditions.

.....

- (ii) Calculate a value for the rate constant under these new conditions and state its units.

*Calculation* .....

.....

.....

*Units* .....

- (iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

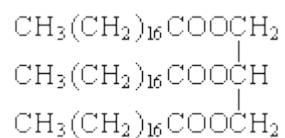
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**(6)**

- (d) A naturally-occurring triester, shown below, was heated under reflux with an excess of aqueous sodium hydroxide and the mixture produced was then distilled. One of the products distilled off and the other was left in the distillation flask.



- (i) Draw the structure of the product distilled off and give its name.

*Structure*

*Name* .....

- (ii) Give the formula of the product left in the distillation flask and give a use for it.

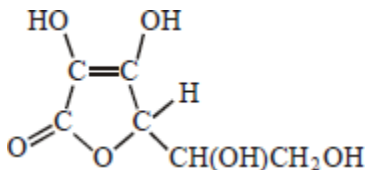
Formula .....

Use .....

(4)  
(Total 15 marks)

7

Which one of the following is **not** a correct statement about vitamin C, shown below?



- A It is a cyclic ester.  
B It can form a carboxylic acid on oxidation.  
C It decolourises a solution of bromine in water.  
D It is a planar molecule.

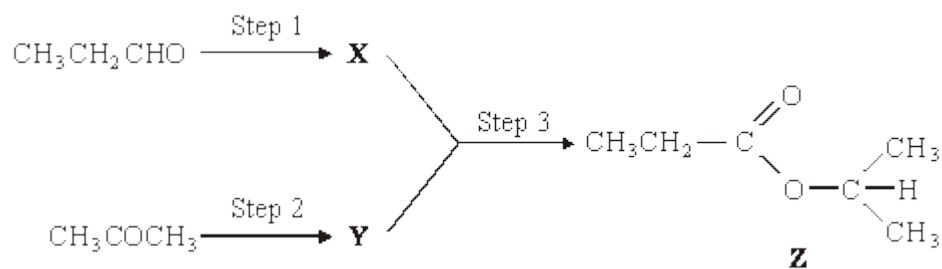
(Total 1 mark)

8

- (a) Describe how propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ , and propanone,  $\text{CH}_3\text{COCH}_3$ , can be distinguished using
- (i) a chemical test and  
(ii) the number of peaks in their proton n.m.r. spectra.

(5)

- (b) Compound **Z** can be produced by the reaction of compound **X** with compound **Y** as shown in the synthesis outlined below.



Identify compounds **X** and **Y**.

For each of the three steps in the synthesis, name the type of reaction involved and give reagents and conditions. Equations are **not** required.

**(10)**  
**(Total 15 marks)**

**9** Propanoic acid reacts with methanol in the presence of a small amount of concentrated sulphuric acid. The empirical formula of the ester formed is

- A**  $\text{CH}_2\text{O}$
- B**  $\text{C}_2\text{H}_6\text{O}_2$
- C**  $\text{C}_2\text{H}_4\text{O}_2$
- D**  $\text{C}_2\text{H}_4\text{O}$

**(Total 1 mark)**