Surname	Centre Number	Candidate Number
Other Names		2

GCE A LEVEL – NEW

A410U20-1

S17-A410U20-1

CHEMISTRY – A level component 2
Organic Chemistry and Analysis

MONDAY, 19 JUNE 2017 – MORNING

2 hours 30 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 7.**	**15**	
Section B	**8.**	**16**	
	9.	**18**	
	10.	**21**	
	11.	**9**	
	12.	**21**	
	13.	**20**	
	Total	**120**	

A410U201
01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (15 marks)** and **Section B (105 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 120.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.10***(f)* and **Q.12***(c)*.

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

SECTION A

Answer **all** *questions in the spaces provided.*

1. Ethane reacts with chlorine by free radical substitution. Explain why ultraviolet light is needed for this reaction and give an equation for the formation of chloroethane. [2]

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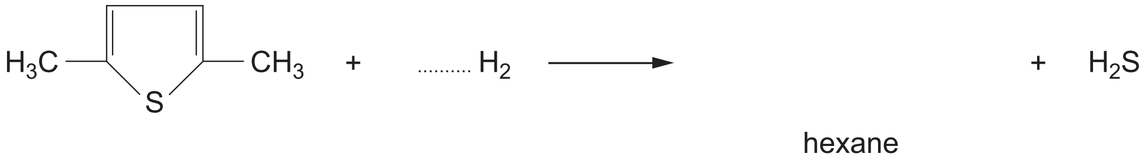
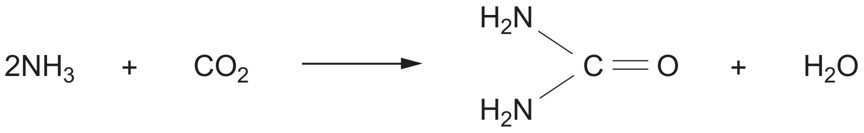
2. Organic sulfur compounds that are present in petroleum need to be removed before it is refined into fuels. They are removed by passing them, together with hydrogen, over a catalyst.
For example



Give the formula of hexane and then balance the equation. [2]

3. The amide urea, $CO(NH_2)_2$, is made in industry by reacting ammonia and carbon dioxide.



(a) Calculate the percentage by mass of nitrogen in urea. [2]

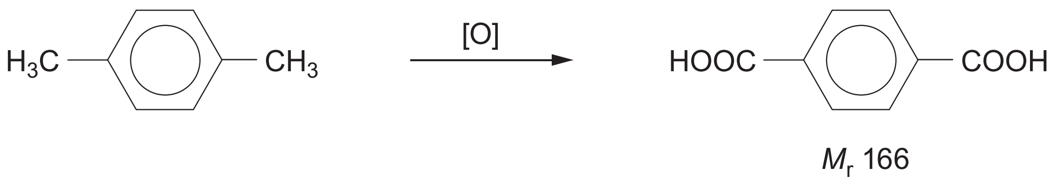
Percentage = ... %

(b) Suggest a reagent that could be used to produce ammonia from the amide urea, when the mixture is heated. [1]

....

Examiner only

4. 1,4-Dimethylbenzene was oxidised to benzene-1,4-dicarboxylic acid.



(a) State a suitable oxidising agent, used in alkaline solution, for this reaction. [1]

....

(b) A by-product of this reaction was a compound with a relative molecular mass of 150. This compound was able to reduce Fehling's solution. Suggest a displayed formula for this compound, giving a reason for your answer. [2]

....

....

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5. Draw the displayed formula of the compound that has the same molecular formula as ethanal, CH_3CHO. [1]

Examiner only

6. Draw a dot and cross diagram of the hydroxide ion. [1]

7. A sample of 1-butyl butanoate (boiling temperature 164 °C) is contaminated with around 10 % of butanoic acid (boiling temperature 162 °C). Describe how you would obtain a pure sample of 1-butyl butanoate from this mixture. [3]

....

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15

SECTION B

Answer **all** *questions in the spaces provided.*

8. *(a)* Ethanedioic acid, $(COOH)_2$, was first produced by the oxidation of carbohydrates with concentrated nitric acid more than 200 years ago. An equation showing the oxidation of sucrose by this method is shown below.

$$C_{12}H_{22}O_{11} + 12HNO_3 \longrightarrow 6(COOH)_2 + 12NO + 11H_2O$$

In a laboratory experiment 25.0 g of sucrose [M_r 342] were added to an excess of concentrated nitric acid, together with a suitable catalyst, in a 1 dm^3 conical flask. The mixture was gently warmed to start the reaction and the rate of the exothermic reaction was controlled by appropriate cooling.

(i) Suggest a simple method of heating and subsequent cooling of the reaction mixture. [1]

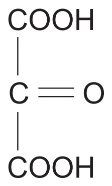
....

....

(ii) After 24 hours, the crystals of ethanedioic acid produced were filtered off, recrystallised and weighed. 18.0 g of ethanedioic acid dihydrate, $(COOH)_2.2H_2O$ [M_r 126], were obtained. Calculate the percentage yield of the dihydrate. [2]

Percentage yield = ... %

(iii) A by-product of the reaction was oxopropanedioic acid.



oxopropanedioic acid

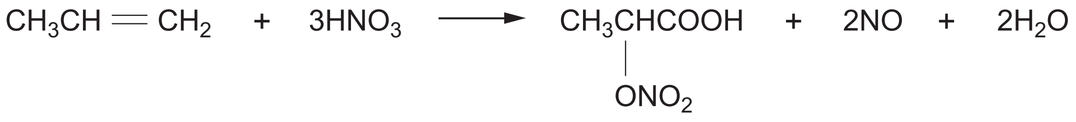
State and explain how the ^{13}C NMR spectrum of this compound would differ from that of ethanedioic acid. [2]

....

....

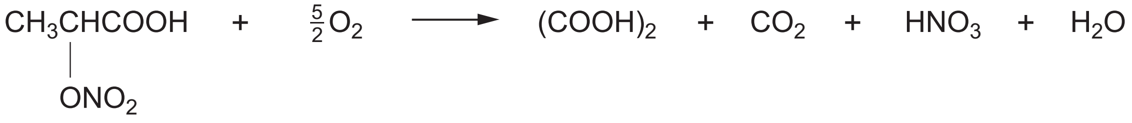
....

(b) Another method to produce ethanedioic acid uses propene from the petrochemical industry as the starting material. Propene is reacted with nitric acid to give an intermediate, which is then treated with oxygen in a second stage. The nitrogen oxides are then oxidised and the product recycled.



$$CH_3CH{=}CH_2 + 3HNO_3 \longrightarrow CH_3CH(ONO_2)COOH + 2NO + 2H_2O$$

intermediate



$$CH_3CH(ONO_2)COOH + \tfrac{5}{2}O_2 \longrightarrow (COOH)_2 + CO_2 + HNO_3 + H_2O$$

Combine these two equations to give an overall equation. [2]

....

(c) A summary of these two industrial processes to make ethanedioic acid is shown in the table.

Method	Organic starting materials	Reaction temperature / °C	Percentage yield / %
1	carbohydrates	< 100	65
2	propene	< 100	90

Give **two** advantages of using method 1. [2]

1. ....

....

2. ....

....

(d) Many vegetables contain ethanedioic acid or its salts. In an experiment 140 g of Brussels sprouts were treated to produce a solution containing ethanedioic acid. Aqueous calcium hydroxide was added to this solution to precipitate insoluble calcium ethanedioate, which was filtered off, washed and dried. It was then heated strongly to give 0.400 g of calcium carbonate.

$$\underset{M_r\ 126}{(COOH)_2.2H_2O} \xrightarrow{Ca(OH)_2} \underset{M_r\ 128}{(COO)_2Ca} \xrightarrow{\text{strong heating}} \underset{M_r\ 100}{CaCO_3}$$

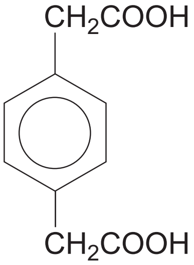
Calculate the mass of ethanedioic acid dihydrate, $(COOH)_2.2H_2O$ in 100 g of Brussels sprouts, giving your answer to an appropriate number of significant figures. [3]

Mass = ... g *(e)* Group 2 salts of dicarboxylic acids undergo decarboxylation on heating. For example, strontium ethanedioate [M_r 176] produces strontium carbonate and carbon monoxide.

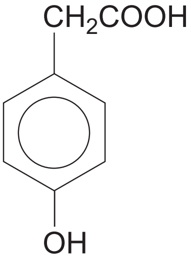
$$(COO)_2Sr \longrightarrow SrCO_3 + CO$$

In an experiment 0.440 g of strontium ethanedioate were heated and produced 61.3 cm^3 of carbon monoxide measured at 298 K and 1 atm pressure. Use these figures to confirm that the starting material was pure strontium ethanedioate. [1]

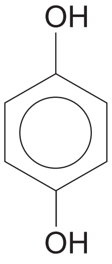
(f) A solution contains either compound **A**, compound **B** or compound **C**.



compound **A**



compound **B**



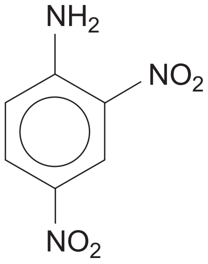
compound **C**

It is possible to identify the compound by using only aqueous bromine and sodium hydrogencarbonate. Complete the table by showing the observations that are made when the compounds are added separately to each reagent. Write ‘no reaction’ if no change is observed. [3]

Reagent	Compound **A**	Compound **B**	Compound **C**
aqueous bromine			
sodium hydrogencarbonate			

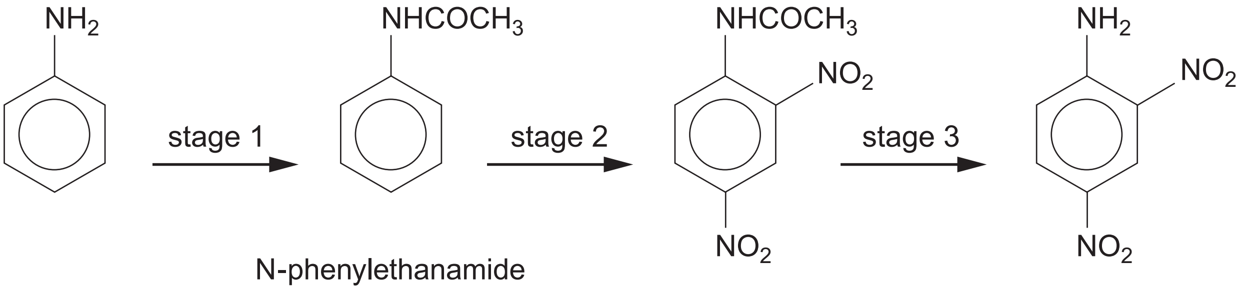
16

9. *(a)* Derivatives of 2,4-dinitrophenylamine have been used as herbicides for about 80 years.



2,4-dinitrophenylamine

One method of preparing this compound is from phenylamine.



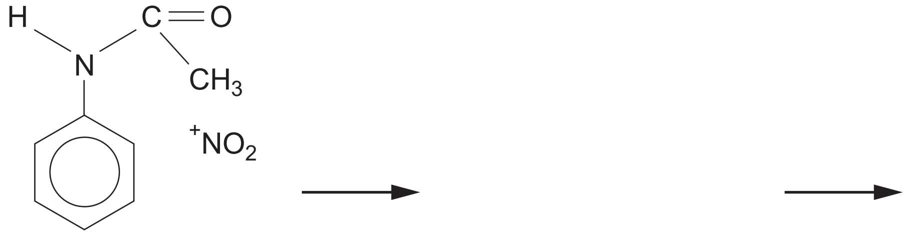
N-phenylethanamide

(i) State the reagent used in stage 1 to produce N-phenylethanamide from phenylamine. [1]

....

(ii) N-phenylethanamide is nitrated by using a mixture of concentrated nitric and sulfuric acids, in the same way as in the nitration of benzene.

Complete the mechanism below to produce 2-nitro-N-phenylethanamide, where just one nitro group has been substituted into the ring. You should include curly arrows, appropriate charges and the formulae of the intermediate and final products. [3]



(iii) By analogy with the nitration of benzene suggest how you could modify the nitration reaction in (ii) to ensure that the dinitro- product is formed. [1]

....

....

(iv) 2,4-Dinitrophenylamine has a melting temperature of 180 °C and is recrystallised from a 1:1 mixture of ethanol and water. Outline the essential stages of this recrystallisation process so that pure dry crystals of 2,4-dinitrophenylamine are obtained. You should assume that a hot water bath is available for use. [4]

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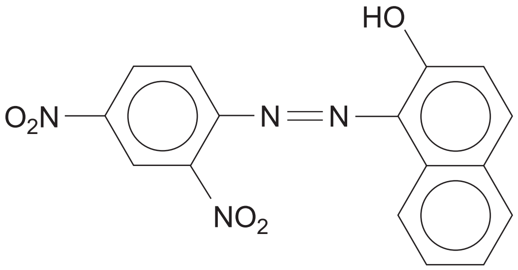
(b) Another use for 2,4-dinitrophenylamine is in the preparation of the azo dye ‘Permanent Red 2G’.



Permanent Red 2G

This is prepared from the diazotisation of 2,4-dinitrophenylamine and then coupling the product with naphthalen-2-ol.

(i) State the reagents and conditions used to produce an aqueous solution of 2,4-dinitrobenzenediazonium chloride from 2,4-dinitrophenylamine. [2]

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....

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(ii) Permanent Red 2G appears red in white light. State and explain the colour observed, if any, when Permanent Red 2G is viewed in

I. blue light [1]

....

....

II. red light [1]

....

....

(c) There are environmental concerns about the use of herbicides based on 2,4-dinitrophenylamine. Naturally-occurring herbicides, such as limonene, are considered to be more acceptable. Limonene is an unsaturated compound that contains two carbon-carbon double bonds in each molecule.

(i) In an experiment 4.08 g of limonene just removed the colour from 9.58 g of bromine. Use this information to calculate the relative molecular mass of limonene. [3]

M_r = ...

(ii) When limonene reacts completely with hydrogen under suitable conditions, menthane is produced. Use information from the question and your answer to part (i) to find the relative molecular mass of menthane. Explain your answer. [2]

M_r = ...

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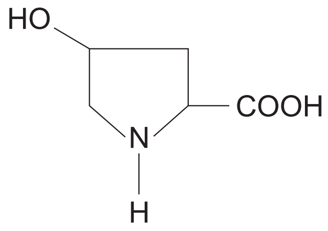
10. *(a)* Hydroxyproline is a cyclic α-amino acid that is produced in the liver. It is an essential part of the muscle protein collagen.



hydroxyproline

(i) Explain why the melting temperature of hydroxyproline is about 240 °C, which is much higher than expected from the formula given. [2]

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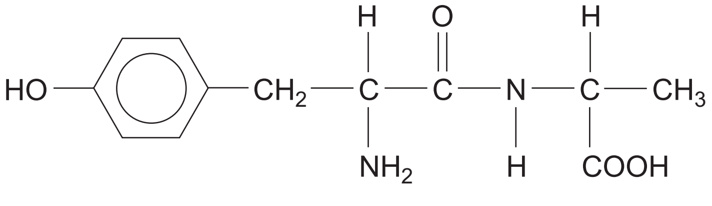
(ii) Give the displayed formula of the compound formed when hydroxyproline has acted as a base. [1]

(b) The formula of a dipeptide formed between 2-aminopropanoic acid and another amino acid is shown below.



Give the displayed formula of the amino acid that forms this dipeptide with 2-aminopropanoic acid. [1]

(c) Secondary protein structure is concerned with hydrogen bonding between certain groups. State the groups present that take part in this hydrogen bonding and explain why it occurs. [2]

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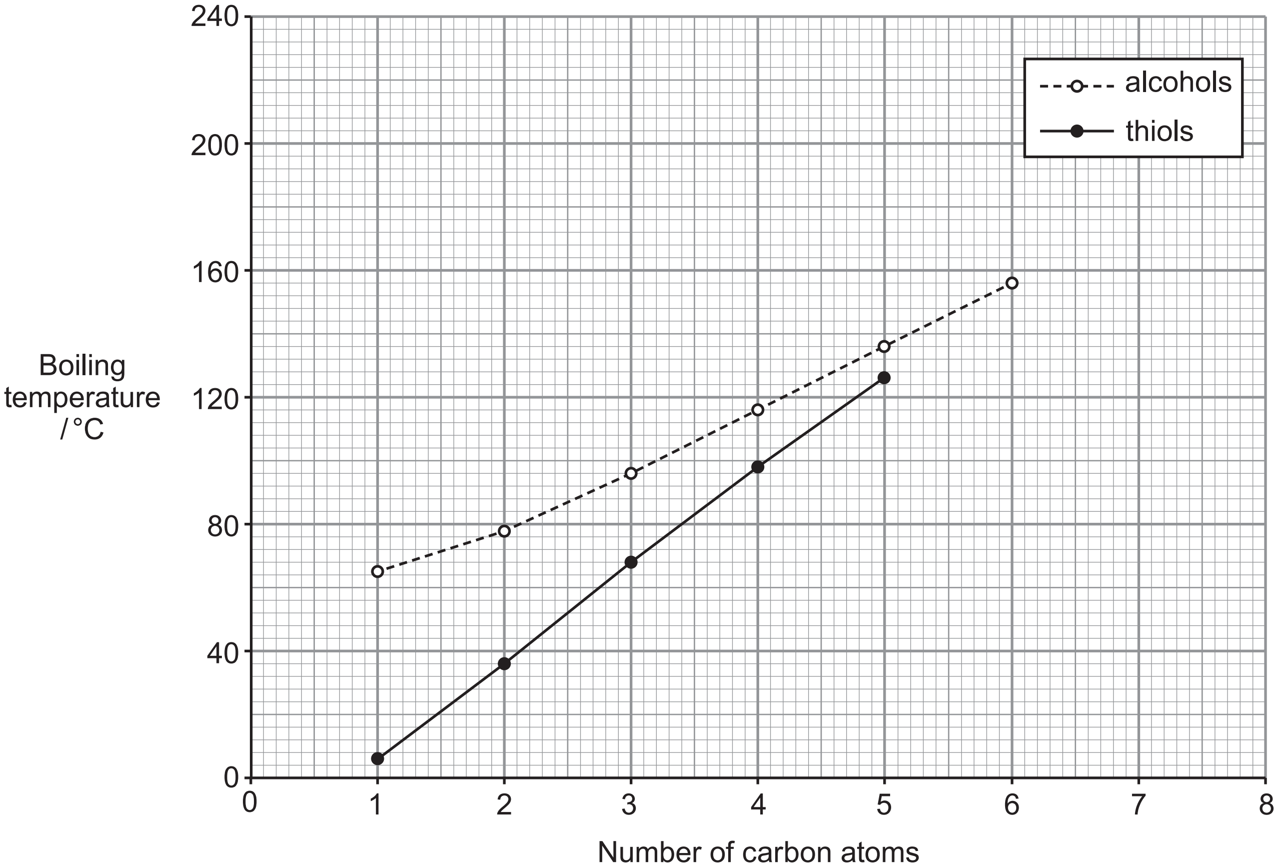
(d) The graph shows the boiling temperatures of some unbranched primary alcohols, R–OH, and those of the corresponding unbranched primary thiols, R–SH.



(i) Explain why the boiling temperature of methanol is higher than would be suggested by the trend in other alcohols. [3]

(ii) Explain why the boiling temperatures of the thiols are lower than the boiling temperatures of the corresponding alcohols. [2]

Turn over.

(e) There are two common methods of producing 1-butyl ethanoate. Butan-1-ol can be reacted with either ethanoyl chloride or ethanoic acid. Both of these reactions can be considered as equilibrium reactions.

$$CH_3CH_2CH_2CH_2OH(l) \quad + \quad CH_3COCl(l) \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3(l) \quad + \quad HCl(g)$$

$$CH_3CH_2CH_2CH_2OH(l) \quad + \quad CH_3COOH(l) \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3(l) \quad + \quad H_2O(l)$$

(i) Use the equations to suggest why the method using ethanoyl chloride gives a higher yield of 1-butyl ethanoate than the method using ethanoic acid. [3]

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(ii) Suggest **one** practical disadvantage of the method that uses ethanoyl chloride. [1]

....

....

(f) Compound **J** is a polyamide that is produced from two different monomers. This polyamide is hydrolysed by boiling it with aqueous sodium hydroxide. After acidifying the mixture obtained from hydrolysis, compound **K**, a dicarboxylic acid of general formula $HOOC–(CH_2)_n–COOH$ is isolated from the mixture. 1.24 g of compound **K** is titrated against aqueous sodium hydroxide of concentration 0.500 mol dm^{-3}. 37.55 cm^3 are needed to just neutralise the acid.

Compound **L** is also formed from hydrolysis of the polyamide. It is a diamine, $H_2N–R–NH_2$, where R is a group containing only carbon and hydrogen. 0.500 g of this diamine reacts with nitric(III) acid to produce 278 cm^3 of nitrogen gas, measured at 298 K and 1 atm.

$$H_2N-(C_x H_{2x})-NH_2 \xrightarrow{\text{nitric (III) acid}} 2N_2 \quad + \quad \text{other products}$$

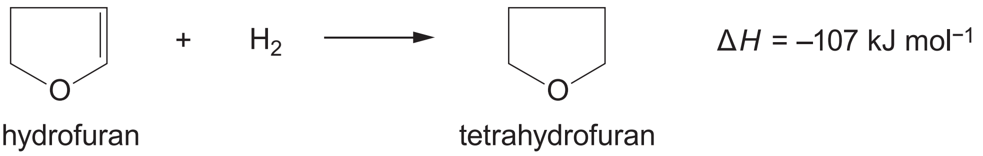
The ^{13}C NMR spectrum of compound **L** shows that the R group contains three different carbon environments.

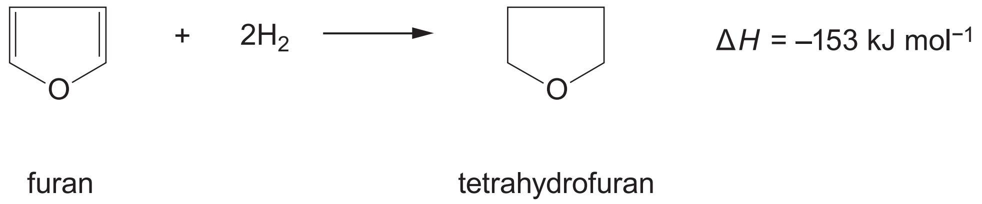
Use the information provided to deduce the displayed formulae of compounds **K** and **L**, and hence give the formula of the repeating section of polyamide **J**. [6 QER]

21

11. (a) Furan, C_4H_4O, is a cyclic compound that contains one oxygen atom as part of the ring.

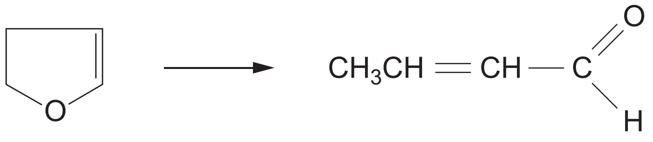
(i) The enthalpies of hydrogenation of dihydrofuran and furan are shown below.





The hydrogenation of a carbon to carbon double bond in furan compounds produces 107 kJ mol^{-1} in an exothermic reaction. Use the information above to calculate the difference between the calculated hydrogenation enthalpy value for furan and the actual value. Suggest a reason for this difference in values. [2]

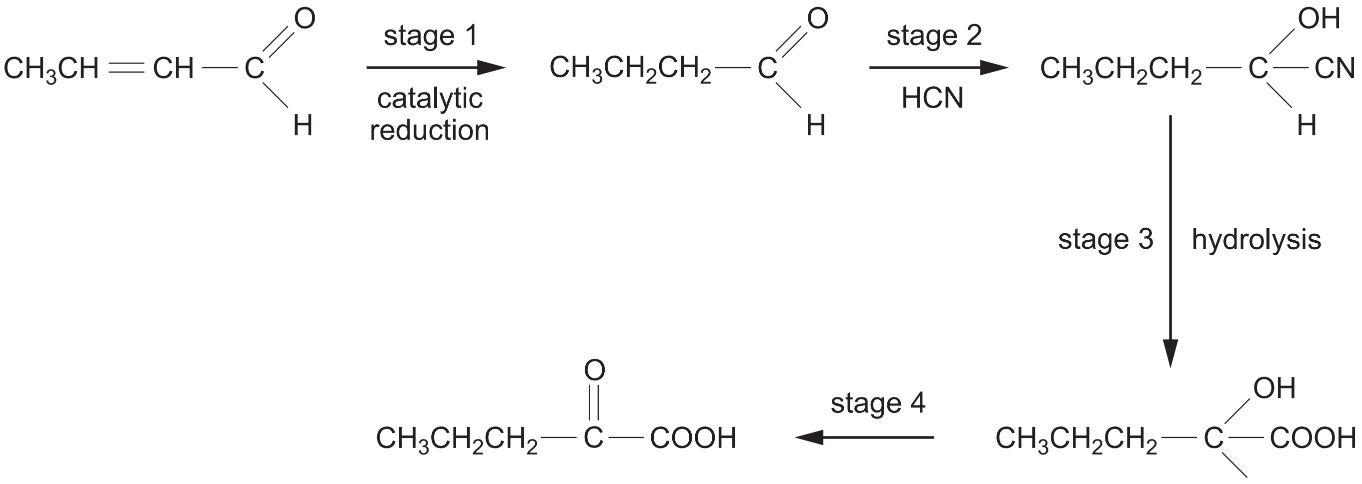
(ii) When dihydrofuran is heated, ring opening occurs giving but-2-enal as one of the products.



$CH_3CH{=}CH{-}CHO$

The reaction products were treated with a solution of 2,4-dinitrophenylhydrazine. State what would be seen and how the product from the reaction with 2,4-dinitrophenylhydrazine could be used to identify but-2-enal. [2]

(b) But-2-enal can be used to prepare 2-oxopentanoic acid by a sequence of reactions.



2-oxopentanoic acid

(i) Suggest an alternative product that might form when but-2-enal is reduced in stage 1. [1]

....

....

(ii) The reaction shown in stage 1 does not always go to completion and some but-2-enal may remain in the reaction mixture. Explain how you could use the infrared spectrum of the mixture to show the presence of any remaining but-2-enal. [1]

....

....

....

(iii) State the type of reaction mechanism occurring during stage 2. [1]

....

(iv) State the type of reaction occurring in stage 4 and give a suitable reagent(s) for this reaction. [2]

Type of reaction ....

Reagent(s) ....

9

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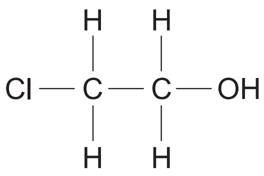
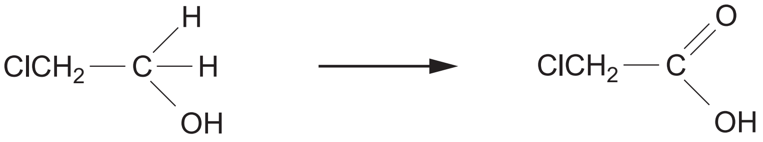
12. *(a)* When ethene is passed into aqueous chlorine one of the products is 2-chloroethanol.



$ClCH_2CH_2OH$

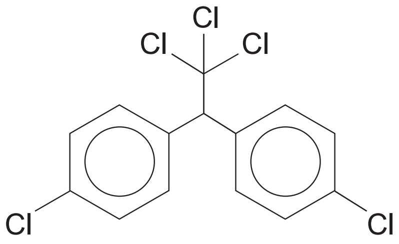
(i) The presence of a C–Cl bond in this compound can be shown by a simple test tube reaction. Outline the practical steps that are used in this method. You can assume that 2-chloroethanol is soluble in water. [4]

(ii) The oxidation of 2-chloroethanol (M_r 80.6) produces chloroethanoic acid together with a little chloroethanal.

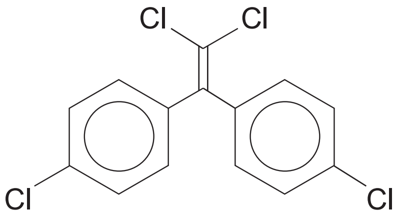


5.80 g of chloroethanol were oxidised and the chloroethanoic acid in the resulting mixture reacted with 0.0600 mol of sodium hydroxide in a 1:1 stoichiometric ratio. Show that the percentage conversion to chloroethanoic acid was 83 %. [3]

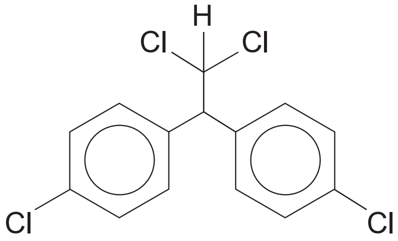
(b) DDT is an effective insecticide but its use in recent years has become restricted because of its persistence in the environment. The DDT that is sold is a mixture of closely related compounds that includes DDT, DDE and DDD.



DDT



DDE

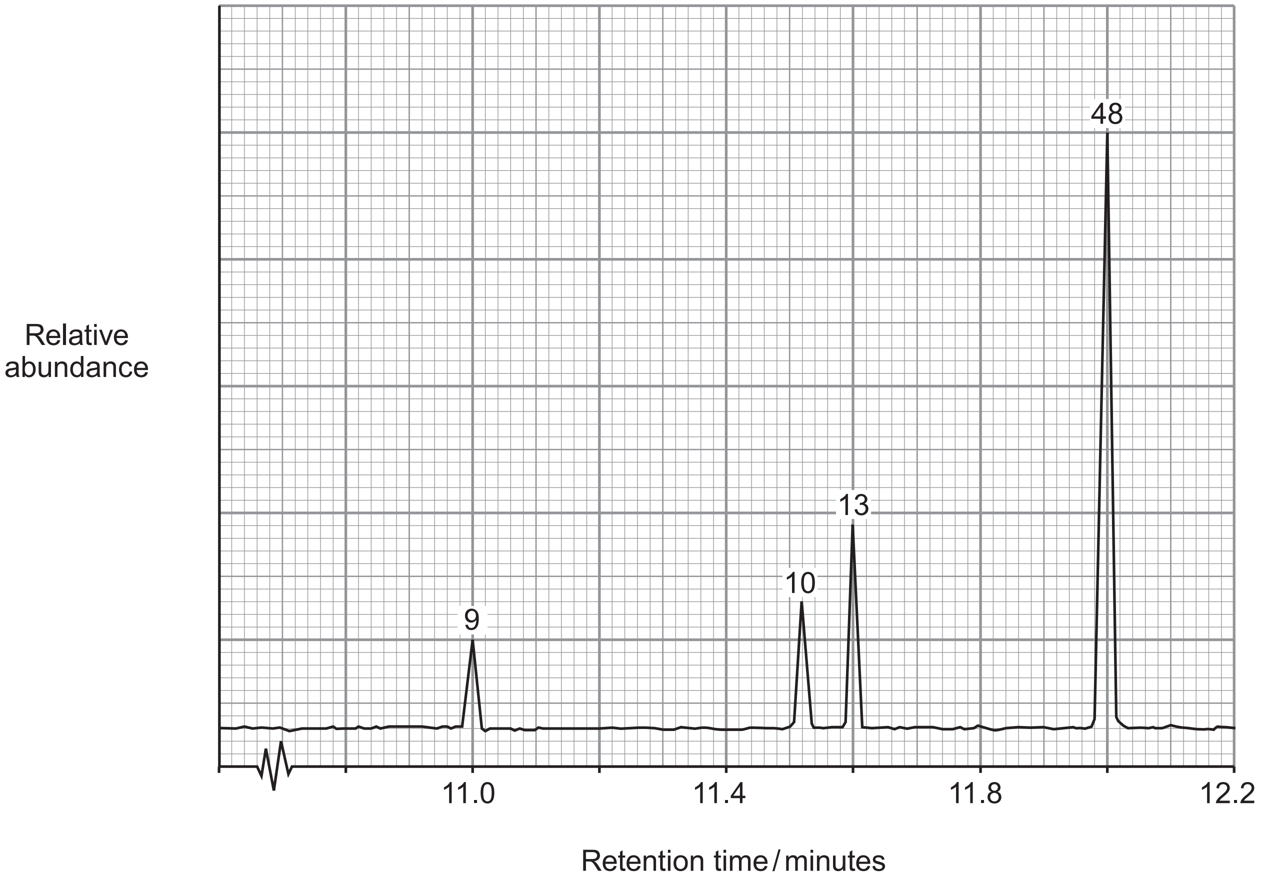


DDD

(i) Suggest why DDT is largely insoluble in water. [1]

(ii) Suggest suitable reagent(s) that can be used to convert DDE into DDD. [1]

(iii) Many areas around former DDT manufacturing sites remain contaminated. The soil from one contaminated area was analysed by gas chromatography.



Calibration of the chromatogram showed that the concentration of DDT in the sample (shown as the largest peak) was 0.018 mol kg^{-1}.

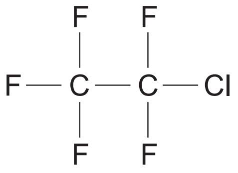
Calculate the **total** concentration of all the contaminants shown in the chromatogram in mol kg^{-1}. [2]

Total concentration = ... mol kg^{-1}

(c) Over the last thirty years the production and use of CFCs has declined mainly because of their adverse environmental effects. Using fluorotrichloromethane as your example, outline how the compound causes a reduction in the amount of ozone present in the upper atmosphere and state **two** problems that can be caused by this reduction.

[6 QER]

(d) The formula of chloropentafluoroethane is shown below.



$$\begin{array}{ccccccc} & & F & & F & & \\ & & | & & | & & \\ F & — & C & — & C & — & Cl \\ & & | & & | & & \\ & & F & & F & & \end{array}$$

State and explain what you would expect to see in the molecular ion region of its mass spectrum and in its ^{13}C spectrum. [4]

21

13. *(a)* 2,3-Dihydroxypropanal (glyceraldehyde), $HOCH_2CH(OH)CHO$, contains a chiral centre.

(i) State what is meant by a *chiral centre*. [1]

....

....

(ii) Draw the two mirror image forms of 2,3-dihydroxypropanal. [1]

(b) Glucose, like 2,3-dihydroxypropanal, contains an aldehyde group.
Fehling's / Benedict's solutions are used to show the presence of an aldehyde.

Describe another simple test to show the presence of this group.
You should include the reagent(s) used and any observations made. [2]

....

....

....

(c) Glucose occurs as two enantiomers. The concentration of an enantiomer can be found by using a polarimeter to measure the rotation of the plane of plane polarised light.
In an experiment using an aqueous solution of D-glucose at a certain temperature, the initial rotation of the plane of plane polarised light was 20° using a cell of 1 dm length to hold the glucose solution.

Use the formula below to calculate the concentration of glucose in the solution in g dm^{-3}. [2]

$$[\alpha_D] = \frac{r \times v}{m}$$

where

specific rotation at this temperature $[\alpha_D]$ = 112°
rotation of the plane of plane polarised light (r) = 20°
volume of solution in 1 dm cell (v) = 15 cm^3

m is the mass of glucose in 15 cm^3 of solution

Concentration = ... g dm^{-3}

(d) Butan-2-ol (M_r 74) can be dehydrated to but-1-ene and but-2-ene.

$$\underset{}{CH_3CH_2CH(OH)CH_3} \longrightarrow \underset{\text{around } 30\,\%}{CH_3CH_2CH{=}CH_2} + \underset{\text{around } 70\,\%}{CH_3CH{=}CHCH_3}$$

(i) State a dehydrating agent for this reaction. [1]

....

(ii) Both but-2-ene and penta-1,3-diene can exist as *E-Z* isomers. Explain why this type of isomerism occurs and give the displayed formula of *E*-penta-1,3-diene. [2]

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(e) Compound **R** is a neutral saturated aliphatic compound that contains only carbon, hydrogen and oxygen. The percentage of oxygen by mass is 24.6. This compound is hydrolysed in acid solution to give two new organic compounds, **S** and **T**. Further information about **R**, **S** and **T** is given below.

Compound **R**

- The ^{13}C NMR spectrum shows that there are five different carbon environments
- The ^{1}H NMR spectrum shows the following signals

Signal δ/ppm	Relative peak area
1.20 singlet	9
1.25 triplet	3
4.11 quartet	2

- The infrared absorption spectrum shows a peak at 1731 cm^{-1} but no peak at 2500–3550 cm^{-1}
- It is not an aldehyde or a ketone

Compound **S**

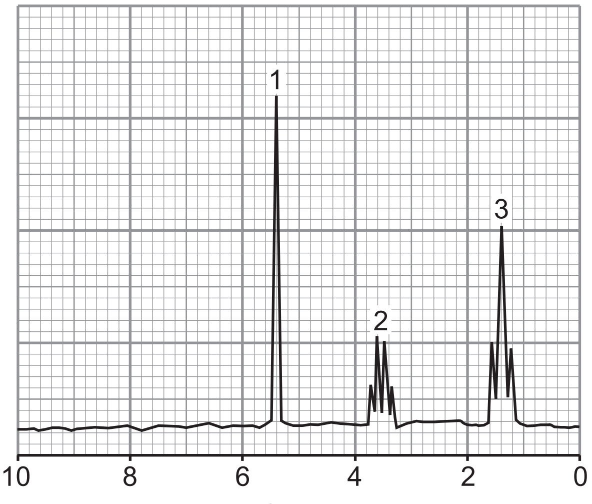
- The ^{13}C NMR spectrum shows that there are three different carbon environments
- The ^{1}H NMR spectrum shows the following signals

Signal δ/ppm	Relative peak area
1.20 singlet	9
around 11	1

- An aqueous solution is weakly acidic

Compound **T**

- The ^{13}C NMR spectrum shows that there are two different carbon environments
- The ^{1}H NMR spectrum is shown below – relative peak areas 1, 2 and 3



- The compound is neutral

Use this information to deduce the formulae of compounds **S** and **T** and hence the displayed formula of compound **R**.

It is not necessary to name any of the compounds. [11]

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END OF PAPER

For continuation only.

Examiner only