**Q1.**          Spectral data for use in this question are provided below the Periodic Table (first item on the database).

Compound **Q** has the molecular formula C4H8O2

(a)     The infra-red spectrum of **Q** is shown below.



Identify the type of bond causing the absorption labelled **R** and that causing the absorption labelled **S**.

***R*** *.*.................................................................................................................

***S***...................................................................................................................

**(2)**

(b)     **Q** does not react with Tollens’ reagent or Fehling’s solution. Identify a functional group which would react with these reagents and therefore cannot be present in **Q**.

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**(1)**

(c)     Proton n.m.r. spectra are recorded using a solution of a substance to which tetramethylsilane (TMS) has been added.

(i)      Give two reasons why TMS is a suitable standard.

*Reason 1 ............................................................................................*

*Reason 2* .............................................................................................

(ii)     Give an example of a solvent which is suitable for use in recording an n.m.r. spectrum. Give a reason for your choice.

*Solvent* ................................................................................................

*Reason* ................................................................................................

**(4)**

(d)     The proton n.m.r. spectrum of **Q** shows 4 peaks.

The table below gives δ values for each of these peaks together with their splitting patterns and integration values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| δ/ppm | 2.20 | 2.69 | 3.40 | 3.84 |
| Splitting pattern | singlet | triplet | singlet | triplet |
| Integration value | 3 | 2 | 1 | 2 |

What can be deduced about the structure of **Q** from the presence of the following in its n.m.r. spectrum?

(i)      The singlet peak at δ = 2.20

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(ii)     The singlet peak at δ = 3.40

.............................................................................................................

(iii)     Two triplet peaks

.............................................................................................................

**(3)**

(e)     Using your answers to parts (a), (b) and (d), deduce the structure of compound **Q**.

**(1)**

**(Total 11 marks)**

**Q2.**          (a)     Draw the structure of ethyl propanoate.

**(1)**

(b)     Name and outline a mechanism for the formation of ethyl propanoate from propanoyl chloride and ethanol.

*Name of mechanism* ....................................................................................

*Mechanism*

**(5)**

(c)     The mass spectrum of ethyl propanoate contains a major peak at *m/z* = 57. Write an equation showing the fragmentation of the molecular ion to form the species responsible for the peak at *m/z* = 57. Show the structure of this species in your answer.

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**(2)**

(d)     Draw the structure of another ester which is an isomer of ethyl propanoate and which gives a major peak at *m/z* = 71 in its mass spectrum.

**(1)**

**(Total 9 marks)**

**Q3.**          Three sections of the proton n.m.r. spectrum of CH3CHClCOOH are shown below.



(a)     Name the compound CH3CHClCOOH

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**(1)**

(b)     Explain the splitting patterns in the peaks at δ 1.72 and δ 4.44

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**(2)**

(c)     Predict the splitting pattern that would be seen in the proton n.m.r. spectrum of the isomeric compound ClCH2CH2COOH

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**(1)**

(d)     The amino acid *alanine* is formed by the reaction of CH3CHClCOOH with an excess of ammonia. The mechanism is nucleophilic substitution. Outline this mechanism, showing clearly the structure of *alanine*.

**(5)**

(e)     The amino acid *lysine* has the structure



Draw structures to show the product formed in each case when lysine reacts with

(i)      an excess of aqueous HCl,

(ii)     an excess of aqueous NaOH,

(iii)     another molecule of lysine.

**(3)**

**(Total 12 marks)**

**Q4.**          The conversion of compound **A** into compound **B** can be achieved in two steps as shown below.



The intermediate compound, **X,** has an absorption at 1650 cm–1 in its infra-red spectrum.

(a)     Identify compound **X**. Explain your answer.

**(2)**

(b)     For each step in this conversion, give the reagents and essential conditions required and outline a mechanism.

**(11)**

(c)     Show how the number of peaks in their proton n.m.r. spectra would enable you to distinguish between compounds **A** and **B**.

**(2)**

**(Total 15 marks)**

**Q5.**         (a)     Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using a simple test-tube reaction for each pair.

(i)      

(ii)     

(iii)     

**(8)**

(b)     State how compounds **E** and **F** in part (a)(iii) above could be distinguished by their infra-red spectra, without using the fingerprint region.  Explain how *fingerprinting* is used to identify a compound.

**(3)**

(c)     Suggest the structure of the fragment responsible for the major peak in the mass spectrum of compound **E** and state its *m/z* value.  Write an equation showing the formation of this fragment from the molecular ion.

**(4)**

**(Total 15 marks)**

**Q6.**          The proton n.m.r. spectrum of compound **X** is shown below.



Compound **X**, C7H12O3, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Chemical shift, δ/ppm | 4.13 | 2.76 | 2.57 | 2.20 | 1.26 |
| Integration ratio | 0.8 | 0.8 | 0.8 | 1.2 | 1.2 |

Refer to the spectrum, the information given above and the data below the Periodic Table provided to answer the following questions.

(a)     How many different types of proton are present in compound **X**?

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**(1)**

(b)     What is the whole-number ratio of each type of proton in compound **X**?

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**(1)**

(c)     Draw the part of the structure of **X** which can be deduced from the presence of the peak at δ2.20.

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**(1)**

(d)     The peaks at δ4.13 and δ1.26 arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

*Alkyl group* ....................................................................................................

*Explanation* ...................................................................................................

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**(3)**

(e)     Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at δ2.76 and δ2.57.

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**(1)**

(f)      Deduce the structure of compound **X**.

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**(2)**

**(Total 9 marks)**

**Q7.**          Use the data given on the back of the Periodic Table (PT) to help you answer this question.
Compounds **A** to **G** are all isomers with the molecular formula C6H12O2

(a)     Isomer **A**, C6H12O2, is a neutral compound and is formed by the reaction between compounds **X** and **Y** in the presence of a small amount of concentrated sulphuric acid.
**X** and **Y** can both be formed from propanal by different redox reactions.
**X** has an absorption in its infra-red spectrum at 1750 cm–1.
Deduce the structural formulae of **A**, **X** and **Y**. Give suitable reagents, in each case, for the formation of **X** and **Y** from propanal and state the role of concentrated sulphuric acid in the formation of **A**.

**(7)**

(b)     Isomers **B**, **C**, **D** and **E** all react with aqueous sodium carbonate to produce carbon dioxide.
Deduce the structural formulae of the three isomers that contain an asymmetric carbon atom.
The fourth isomer has only three singlet peaks in its proton n.m.r. spectrum. Deduce the structural formula of this isomer and label it **E**.

**(4)**

(c)     Isomer **F**, C6H12O2, has the structural formula shown below, on which some of the protons have been labelled.



A proton n.m.r. spectrum is obtained for **F**. Using Table 1 at the back of the Periodic Table (PT), predict a value of δ for the protons labelled *a* and also for those labelled *b*. State and account for the splitting patterns of the peaks assigned to the protons *a* and *b*.

**(6)**

(d)     Isomer **G**, C6H12O2, contains six carbon atoms in a ring. It has an absorption in its infra-red spectrum at 3270 cm–1 and shows only three different proton environments in its proton n.m.r. spectrum. Deduce a structural formula for **G**.

**(2)**

**(Total 19 marks)**

**Q8.**          Compound **Q** has the molecular formula C4H7ClO and does not produce misty fumes when added to water.

(a)     The infra-red spectrum of **Q** contains a major absorption at 1724 cm–1. Identify the bond responsible for this absorption.

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**(1)**

(b)     The mass spectrum of **Q** contains two molecular ion peaks at *m*/*z* = 106 and *m*/*z*= 108.
It also has a major peak at *m*/*z* = 43.

(i)      Suggest why there are two molecular ion peaks.

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(ii)     A fragment ion produced from **Q** has *m*/*z* = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

*Fragment ion* .......................................................................................

*Equation* ..............................................................................................

**(3)**

(c)     The proton n.m.r. spectrum of **Q** was recorded.

(i)      Suggest a suitable solvent for use in recording this spectrum of **Q**.

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(ii)     Give the formula of the standard reference compound used in recording proton n.m.r. spectra.

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**(2)**

(d)     The proton n.m.r. spectrum of **Q** shows three peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting pattern.

|  |  |  |  |
| --- | --- | --- | --- |
|   | Peak 1 | Peak 2 | Peak 3 |
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |
| Number of adjacent,non-equivalent protons | 1 |   |   |

**(1)**

(e)     Using the information in parts (a), (b) and (d), deduce the structure of compound **Q**.

**(1)**

(f)      A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

**(1)**

**(Total 9 marks)**

**Q9.**          (a)     Ester **X**, CH3CH2COOCH3, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved.

**(6)**

(b)     The proton n.m.r. spectrum of **X** is shown below together with that of an isomeric ester,**Y**. Deduce which of Spectrum 1 and Spectrum 2 is that obtained from **X**. Use **Table 1** on the Data Sheet and the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.





**(4)**

**(Total 10 marks)**

**Q10.**          Compounds **C** and **D**, shown below, are isomers of C5H10O



**C                                          D**

(a)     Name compound **C**.

......................................................................................................................

**(1)**

(b)     Use **Table 2** on the Data Sheet to help you to answer this question.

(i)      Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **C** but not in that of **D**.

.............................................................................................................

(ii)     Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **D** but not in that of **C**.

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**(2)**

(c)     Deduce the number of peaks in the proton n.m.r. spectrum of **C**.

......................................................................................................................

**(1)**

(d)     Identify a reagent that you could use to distinguish between **C** and **D**. For each of **C** and **D**, state what you would observe when the compound is treated with this reagent.

*Reagent* .......................................................................................................

*Observation with* **C** .......................................................................................

*Observation with* **D**.......................................................................................

**(3)**

(e)     Compound **E**, CH3CH2CH2CH2CHO, is also an isomer of C5H10O

Identify a reagent which will react with **E** but not with **C** or **D**. State what you would observe when **E** is treated with this reagent.

*Reagent* .......................................................................................................

*Observation with* **E** .......................................................................................

**(2)**

**(Total 9 marks)**

**Q11.**          (a)     Describe how propanal, CH3CH2CHO, and propanone, CH3COCH3, 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)**

**Q12.**          Compound **U** is shown below.



(a)     Name compound **U**.

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**(1)**

(b)     (i)      State why the mass spectrum of **U** contains two molecular ion peaks.

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(ii)     Give the *m/z* values of these two peaks.

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**(2)**

(c)     Name and outline a mechanism for the reaction of **U** with CH3OH

*Name of mechanism* ....................................................................................

*Mechanism*

**(5)**

**(Total 8 marks)**

**Q13.**          Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data Sheet where appropriate.

(a)     Compounds **A** and **B** have the molecular formula C5H10**A** decolourises bromine water but **B** does not.

**A**       **B**

**(2)**

(b)     Compounds **C** and **D** have the molecular formula C2H4O2

Each has an absorption in its infra-red spectrum at about 1700 cm–1 but only **D** has a broad absorption at 3350 cm–1

**C**       **D**

**(2)**

(c)     Compounds **E** and **F** are esters with the molecular formula C5 H10O2

The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

**E**       **F**

**(2)**

(d)     Compounds **G** and **H** have the molecular formula C3H6Cl2 **G** shows optical activity but **H** does not.

**G**      **H**

**(2)**

(e)     Compounds **I** and **J** have the molecular formula C6H12

Each has an absorption in its infra-red spectrum at about 1650 cm–1 and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

**I**        **J**

**(2)**

**(Total 10 marks)**

**Q14.**          This question concerns four isomers, **W**, **X**, **Y** and **Z**, with the molecular formula C5H10O2

(a)     The proton n.m.r. spectrum of **W** shows 4 peaks.
The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| δ/ppm  | 2.18  | 2.59  | 3.33  | 3.64  |
| Splitting pattern  | singlet  | triplet  | singlet  | triplet  |
| Integration value  | 3  | 2  | 3  | 2  |

State what can be deduced about the structure of **W** from the presence of the following in its n.m.r. spectrum.

(i)      The singlet peak at δ = 2.18

.............................................................................................................

(ii)     The singlet peak at δ = 3.33

.............................................................................................................

(iii)     Two triplet peaks.

.............................................................................................................

(iv)    Hence, deduce the structure of **W**.

**(4)**

(b)     The infra-red spectrum of **X** is shown below.



(i)      What can be deduced from the broad absorption centred on 3000 cm–1 in the infra-red spectrum of **X**?

.............................................................................................................

(ii)     Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

**(2)**

(c)     Isomers **Y** and **Z** have the structures shown below.



Identify the two reagents you could use in a simple chemical test to distinguish between **Y** and **Z**. State what you would observe when each of **Y** and **Z** is tested with a mixture of these two reagents.

*Reagents* ....................................................................................................

*Observation with* ***Y*** ......................................................................................

*Observation with* ***Z*** .......................................................................................

**(3)**

**(Total 9 marks)**

**Q15.**          (a)     The reaction of but-1-ene with chlorine produces 1,2-dichlorobutane, C4H8Cl2

(i)      Given that chlorine exists as a mixture of two isotopes, 35Cl and 37Cl, predict the number of molecular ion peaks and their *m/z* values in the mass spectrum of C4H8Cl2

(ii)     The mass spectrum of 1,2-dichlorobutane contains peaks at *m/z* = 77 and 79. Draw the structure of the fragment ion which produces the peak at *m/z*= 77 and write an equation showing its formation from the molecular ion.

**(6)**

(b)     The reaction of but-2-ene with hydrogen chloride forms a racemic mixture of the stereoisomers of 2-chlorobutane.

(i)      Name the type of stereoisomerism shown by 2-chlorobutane and give the meaning of the term *racemic mixture*. State how separate samples of the stereoisomers could be distinguished.

(ii)     By considering the shape of the reactive intermediate involved in the mechanism of this reaction, explain how a racemic mixture of the two stereoisomers of 2-chlorobutane is formed.

**(7)**

(c)     The reaction of but-2-ene with chlorine produces 2,3-dichlorobutane, C4H8Cl2

(i)      State the number of peaks, their integration ratio and any splitting of peaks in the proton n.m.r. spectrum of 2,3-dichlorobutane.

(ii)     Compound **S**, an isomer of C4H8Cl2, produces a proton n.m.r. spectrum which consists only of a singlet, a triplet and a quartet with an integration ratio of 3:3:2 respectively.

Compound **T**, also an isomer of C4H8Cl2, produces a proton n.m.r. spectrum which consists only of two singlets with an integration ratio of 3:1

Draw the structures of **S** and of **T**.

**(6)**

**(Total 19 marks)**

**Q16.**          (a)     The infra-red spectrum of compound **A**, C3H6O2, 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 C5H10

Draw the structures of the three dibromoalkanes, C5H10Br2, 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)**

**Q17.**          Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using 13C n.m.r. spectroscopy.



cyclohexan-1,2-diol         cyclohexan-1,3-diol       cyclohexan-1,4-diol

The 13C n.m.r. spectrum of cyclohexan-1,2-diol is shown below.



(a)     (i)      Explain why there are three peaks.

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(ii)     Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for 13C vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan-1,2-diol.

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(b)     (i)      Predict the number of peaks in the 13C n.m.r. spectrum of cyclohexan-1,3-diol.

.............................................................................................................

(ii)     Predict the number of peaks in the 13C n.m.r. spectrum of cyclohexan-1,4-diol.

.............................................................................................................

(c)     Suggest why the structures drawn above represents several stereoisomers.

......................................................................................................................

**(Total 5 marks)**

**Q18.**         It is necessary to use several analytical techniques to determine the structure of an unknown compound.

An analytical chemist was asked to determine the structure of compound **Q** which was found in a waste tank in a mixture of volatile liquids.

Compound **Q** has the molecular formula C4H7ClO. It is a volatile liquid which does not produce misty fumes when added to water.

(a)     Suggest how the chemist could obtain a sample of **Q** for analysis from the mixture of volatile liquids.

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**(1)**

(b)     The infra-red spectrum of Q contains a major absorption at 1724 cm–1. Identify the bond which causes this absorption.

......................................................................................................................

**(1)**

(c)     The mass spectrum of Q contains two molecular ion peaks at *m/z* = 106 and *m/z*= 108.
It also has a major peak at *m/z* = 43.

(i)      Suggest why there are two molecular ion peaks.

.............................................................................................................

(ii)     A fragment ion produced from **Q** has *m/*z = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

*Fragment ion ..*....................................................................................

*Equation* .............................................................................................

**(3)**

(d)     The proton n.m.r. spectrum of **Q** was recorded.

(i)      Suggest a suitable solvent for use in recording this spectrum of **Q**.

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(ii)     Give the formula of the standard reference compound used in recording proton
n.m.r. spectra.

.............................................................................................................

**(2)**

(e)     The proton n.m.r. spectrum of Q shows 3 peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting patterns.

|  |  |  |  |
| --- | --- | --- | --- |
|   | Peak 1 | Peak 2 | Peak 3 |
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |
| Number of adjacent,non-equivalent protons | 1 |   |   |

**(1)**

(f)      Using the information in parts (a), (b) and (d) deduce the structure of compound **Q.**

**(1)**

(g)     A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

**(1)**

**(Total 10 marks)**

**Q19.**         (a)     Alcohols can be classed as primary, secondary or tertiary. Draw possible structures for a primary, a secondary and a tertiary alcohol which have the molecular formula C4H8O.
Which of the structures you have drawn cannot be oxidised by potassium dichromate in acid solution?

**(4)**

(b)     Explain what is meant by the fingerprint region of an infra-red spectrum. State how it is used to confirm the identity of organic molecules such as the primary, secondary and tertiary alcohols of molecular formula C4H8O.

**(2)**

(c)     Each of the parts below concerns a different pair of isomers. Deduce one possible structural formula for each of the species **A** to **F**. Use, where appropriate, the table of infra-red absorption data given on the data sheet.

(i)      **A** and **B** have the molecular formula C3H8O. **A** has a broad absorption band at 3300 cm–1 in its infra-red spectrum, but **B** does not.

(ii)     **C** and **D** have the molecular formula C5H10. **C** has a weak absorption band at 1650 cm–1 in its infra-red spectrum, but **D** does not.

(iii)     **E** and **F** have the molecular formula C3H6O and both have strong absorption bands at about 1700 cm–1 in their infra-red spectra. **E** reacts with Tollens’ reagent but **F** does not.

**(6)**

**(Total 12 marks)**

**Q20.**          Butan-2-ol can be oxidised by acidified potassium dichromate(VI) to form butanone as shown by the following equation.

CH3CH2CH(OH)CH3   +   [O]   →   CH3CH2COCH3   +   H2O

(a)     State the class of alcohol to which butan-2-ol belongs.

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**(1)**

(b)     The infrared spectrum shown below is either that of butan-2-ol or that of butanone.



Identify the compound to which this infrared spectrum refers.

Explain your answer.

You may find it helpful to refer to the table of infrared absorption data on the back of the Periodic Table (**Table 1**).

Identity of the compound .............................................................................

Explanation ..................................................................................................

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**(3)**

(c)     Draw the displayed formula of the alcohol C4H9OH which is resistant to oxidation by acidified potassium dichromate(VI).

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**(1)**

**(Total 5 marks)**

**Q21.**          Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

(a)     Compounds **A** and **B** have the molecular formula C3H6O
**A** has an absorption at 1715 cm–1 in its infrared spectrum and has only one peak in its 1H n.m.r. spectrum.
**B** has absorptions at 3300 cm–1 and at 1645 cm–1 in its infrared spectrum and does **not** show *E–Z* isomerism.

**A                                                    B**

**(2)**

(b)     Compounds **C** and **D** have the molecular formula C5H12In their 1H n.m.r. spectra, **C** has three peaks and **D** has only one.

**C                                                    D**

**(2)**

(c)     Compounds **E** and **F** are both esters with the molecular formula C4H8O2In their 1H n.m.r. spectra, **E** has a quartet at δ = 2.3 ppm and **F** has a quartet at δ = 4.1 ppm.

**E                                                    F**

**(2)**

(d)     Compounds **G** and **H** have the molecular formula C6H12O
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm–1 in its infrared spectrum. **G** forms a silver mirror with Tollens’ reagent but **H** does not.

**G                                                   H**

**(2)**

(e)     Compounds **I** and **J** have the molecular formula C4H11N and both are secondary amines. In their 13C n.m.r. spectra, **I** has two peaks and **J** has three.

**I                                                     J**

**(2)**

**(Total 10 marks)**

**Q22.**          A mass spectrometer can be used to investigate the isotopes in an element.

(a)     Define the term *relative atomic mass* of an element.

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**(2)**

(b)     Element **X** has a relative atomic mass of 47.9

Identify the block in the Periodic Table to which element **X** belongs and give the electron configuration of an atom of element **X**.

Calculate the number of neutrons in the isotope of **X** which has a mass number 49

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**(3)**

(c)     The mass spectrum of element **Z** is shown below.

Use this spectrum to calculate the relative atomic mass of **Z**, giving your answer to one decimal place.

Identify element **Z**.



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**(4)**

(d)     State how vaporised atoms of **Z** are converted into **Z**+ ions in a mass spectrometer.

State and explain which of the **Z**+ ions formed from the isotopes of **Z** in part (c) will be deflected the most in a mass spectrometer.

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**(4)**

(e)     Explain briefly how the relative abundance of an ion is measured in a mass spectrometer.

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**(2)**

**(Total 15 marks)**

**Q23.**          In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

(a)     Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

......................................................................................................................

**(1)**

(b)     The molecular formula of TCDD is C12H4O2Cl4

Chlorine exists as two isotopes 35Cl (75%) and 37Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m/z* value of the most abundant molecular ion peak.

Number of molecular ion peaks ...................................................................

......................................................................................................................

*m/z* value of the most abundant molecular ion peak ...................................

......................................................................................................................

**(2)**

(c)Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

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**(1)**

(d)     TCDD can also be analysed using 13C n.m.r.

(i)      Give the formula of the compound used as the standard when recording a 13C spectrum.

.............................................................................................................

**(1)**

(ii)     Deduce the number of peaks in the 13C n.m.r. spectrum of TCDD.

.............................................................................................................

**(1)**

**(Total 6 marks)**

**Q24.**          Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



(a)     (i)      Draw a **branched-chain** isomer of **A** that exists as optical isomers.

**(1)**

(ii)Name the type of mechanism in Reaction **1**.

.............................................................................................................

**(1)**

(iii)Give the full IUPAC name of compound **B**.

.............................................................................................................

**(1)**

(b)The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**.
Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

(i)

|  |  |
| --- | --- |
|  |  |

(ii)

|  |  |
| --- | --- |
|  |  |

(iii)

|  |  |
| --- | --- |
|  |  |

(iv)

|  |  |
| --- | --- |
|  |  |

**(4)**

(c)Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .................................................................................

**(2)**

(d)     (i)      Outline a mechanism for Reaction **3**.

**(4)**

(ii)     State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

.............................................................................................................

**(1)**

(iii)Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

**(1)**

(e)**D** is a primary amine which has three peaks in its 13C n.m.r. spectrum.

(i)An isomer of **D** is also a primary amine and also has three peaks in its 13C n.m.r. spectrum. Draw the structure of this isomer of **D**.

**(1)**

(ii)Another isomer of **D** is a tertiary amine. Its 1H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

**(1)**

**(Total 17 marks)**

**Q25.**          Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



(a)     Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** .........................................................................

Functional group labelled **K** .........................................................................

**(2)**

(b)     The 1H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the 1H n.m.r. spectrum is produced by the CH2 group labelled *p* in the structure of atenolol.
Use **Table** **2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values .......................................................................................

Name of splitting pattern ……......................................................................

**(2)**

(c)     N.m.r. spectra are recorded using samples in solution.
The 1H n.m.r. spectrum was recorded using a solution of atenolol in CDCl3

(i)      Suggest why CDCl3 and **not** CHCl3 was used as the solvent.

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**(1)**

(ii)     Suggest why CDCl3 is a more effective solvent than CCl4 for polar molecules such as atenolol.

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**(1)**

(d)     The 13C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the
13C n.m.r. spectrum of atenolol.

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**(1)**

(e)     Part of the 13C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



(i)      Give the formula of the compound that is used as a standard and produces the peak at δ = 0 ppm in the spectrum.

.............................................................................................................

**(1)**

(ii)     One of the peaks in the 13C n.m.r. spectrum above is produced by the CH3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

.............................................................................................................

**(1)**

(iii)     There are three CH2 groups in the structure of atenolol. One of these CH2 groups produces the peak at δ = 71 in the 13C n.m.r. spectrum above.
Draw a circle around this CH2 group in the structure of atenolol shown below.



**(1)**

(f)      Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

(i)      Suggest a reducing agent that could reduce a ketone to form atenolol.

.............................................................................................................

**(1)**

(ii)     Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



**(1)**

(iii)     Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

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**(2)**

(iv)    Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage ...........................................................................................

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Disadvantage ......................................................................................

.............................................................................................................

**(2)**

**(Total 16 marks)**

**Q26.**          Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

(a)     The following compounds can be distinguished by observing what happens in test-tube reactions.

For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

(i)



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**(3)**

(ii)



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**(3)**

(iii)



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**(3)**

(b)     Compounds **J** and **K** can also be distinguished using spectroscopic techniques
such as 1H n.m.r.



(i)      Name compound **J**.

Give the total number of peaks in the 1H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

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**(3)**

(ii)     Name compound **K**.

Give the total number of peaks in the 1H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

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**(3)**

**(Total 15 marks)**

**Q27.**          Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



(a)     Give the IUPAC name for phthalic acid.

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**(1)**

(b)     Draw the displayed formula of the repeating unit of poly(chloroethene).

**(1)**

(c)     The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

(i)      Complete the following equation showing the formation of DEP from phthalic anhydride.



**(2)**

(ii)     Deduce the number of peaks in the 13C n.m.r. spectrum of DEP.

.............................................................................................................

**(1)**

(iii)     One of the peaks in the 13C n.m.r. spectrum of DEP is at δ = 62 ppm.

**Table 3** on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



**(1)**

(d)     The mass spectrum of DEP includes major peaks at *m/z* = 222 (the molecular ion) and at *m/z* = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at *m/z* = 177

......................................................................................................................

**(2)**

(e)     Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

An organisation that represents the manufacturers of plasticisers asserts that experimental evidence and research findings show that phthalates do not pose a risk to human health because they biodegrade in a short time scale.

According to the organization’s research, phthalates do not represent a risk for humans or for the environment and they are biodegradable.

(i)      Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

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**(1)**

(ii)     Suggest what needs to be done so that the public could feel confident that the research discussed above is reliable.

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*(Extra space)* .......................................................................................

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**(2)**

**(Total 11 marks)**

**Q28.**          The table below shows the structures of three isomers with the molecular formula C5H10O

|  |  |
| --- | --- |
| Isomer **1** | (*E*)-pent-3-en-2-ol |
| Isomer **2** | pentanal |
| Isomer **3** |   |

(a)     Complete the table by naming Isomer **3**.

**(1)**

(b)     State the type of structural isomerism shown by these three isomers.

.....................................................................................................................

**(1)**

(c)     The compound (*Z*)-pent-3-en-2-ol is a stereoisomer of (*E*)-pent-3-en-2-ol.

(i)      Draw the structure of (*Z*)-pent-3-en-2-ol.

**(1)**

(ii)     Identify the feature of the double bond in (*E*)-pent-3-en-2-ol and that in
(*Z*)-pent-3-en-2-ol that causes these two compounds to be stereoisomers.

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**(1)**

(d)     A chemical test can be used to distinguish between separate samples of Isomer **2** and Isomer **3**.
Identify a suitable reagent for the test.
State what you would observe with Isomer **2** and with Isomer **3**.

Test reagent ...............................................................................................

Observation with Isomer **2**...........................................................................

.....................................................................................................................

Observation with Isomer **3**............................................................................

.....................................................................................................................

**(3)**

(e)     The following is the infrared spectrum of one of the isomers **1**, **2** or **3**.



(i)      Deduce which of the isomers (**1**, **2** or **3**) would give this infrared spectrum. You may find it helpful to refer to **Table 1** on the Data Sheet.

.............................................................................................................

**(1)**

(ii)     Identify two features of the infrared spectrum that support your deduction.
In each case, identify the functional group responsible.

Feature 1 and functional group ...........................................................

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Feature 2 and functional group ...........................................................

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**(2)**

**(Total 10 marks)**

**Q29.**          Mass spectrometry can be used to identify isotopes of elements.

(a)     (i)      In terms of fundamental particles, state the difference between isotopes of an element.

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**(1)**

(ii)     State why isotopes of an element have the same chemical properties.

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**(1)**

(b)     Give the meaning of the term *relative atomic mass.*

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*(Extra space)*.................................................................................................

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**(2)**

(c)     The mass spectrum of element **X** has four peaks. The table below gives the relative abundance of each isotope in a sample of element **X**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *m/z* | 64 | 66 | 67 | 68 |
| Relative abundance | 12 | 8 | 1 | 6 |

(i)      Calculate the relative atomic mass of element **X**.
Give your answer to one decimal place.

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**(3)**

(ii)     Use the Periodic Table to identify the species responsible for the peak at *m/z*= 64

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**(2)**

(d)     Suggest **one** reason why particles with the same mass and velocity can be deflected by different amounts in the same magnetic field.

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**(1)**

(e)     Explain how the detector in a mass spectrometer enables the abundance of an isotope to be measured.

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*(Extra space)* ...............................................................................................

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**(2)**

**(Total 12 marks)**

**Q30.**Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



(a)     The mechanism of the nitration of methylbenzene is an electrophilic substitution.

(i)      Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents ..............................................................................................

...............................................................................................................

Equation ................................................................................................

...............................................................................................................

**(3)**

(ii)     Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

**(3)**

(b)     Deduce the number of peaks in the 13C n.m.r. spectrum of TNT.

........................................................................................................................

**(1)**

(C)     Deduce the number of peaks in the 1H n.m.r. spectrum of TNT.

........................................................................................................................

**(1)**

(d)     Using the molecular formula (C7H5N3O6), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

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**(1)**

**(Total 9 marks)**

**Q31.**Compound **X** (C6H12O2) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

(a)     The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm–1 in the spectrum.

........................................................................................................................

**(1)**

(b)     The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| δ /ppm | 1.2 | 2.2 | 2.6 | 3.8 |
| Integration value | 6 | 3 | 2 | 1 |

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i)      The peak at δ = 2.6

...............................................................................................................

**(1)**

(ii)     The peak at δ = 2.2

...............................................................................................................

**(1)**

(iii)    The peak at δ = 1.2

...............................................................................................................

**(1)**

(iv)     Deduce the structure of **X** (C6H12O2)

**(1)**

**(Total 5 marks)**

**Q32.**Mass spectrometry is used by organic chemists to help distinguish between different compounds.

Four isomers of C9H10O, shown below, were analysed by mass spectrometry.



The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m/z* = 134

The data in the table below show the *m/z* values greater than 100 for the major peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

|  |  |  |
| --- | --- | --- |
| **Spectrum** | ***m/z* values for major peaks** | **No major peak at *m/z*** |
| I | 119 | 133, 105 |
| II | 133, 119 and 105 |   |
| III | 133, 105 | 119 |
| IV | 105 | 133, 119 |

(a)     Two of the molecular ions fragmented to form an ion with *m/z* = 133 by losing a radical.
Identify the radical that was lost.

........................................................................................................................

**(1)**

(b)     Two of the molecular ions fragmented to form an ion with *m/z* = 119 by losing a radical.
Identify the radical that was lost.

........................................................................................................................

**(1)**

(c)     Three of the molecular ions fragmented to form ions with *m/z* = 105 by losing a radical with *M*r = 29

Identify **two** different radicals with *M*r = 29 that could have been lost.

Radical 1 .......................................................................................................

Radical 2 .......................................................................................................

**(2)**

(d)     Consider the structures of the four isomers and the fragmentations indicated in parts (a) to (c).
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

|  |  |
| --- | --- |
| Spectrum I |  |
| Spectrum II |  |
| Spectrum III |  |
| Spectrum IV |  |

**(4)**

**(Total 8 marks)**

**Q33.**Consider the five cyclic compounds, **A**, **B**, **C**, **D** and **E**.



(a)     The infrared spectra of compounds **A**, **B**, **C** and **D** are shown below.

Write the correct letter, **A**, **B**, **C** or **D**, in the box next to each spectrum. You may find it helpful to refer to **Table 1** on the Data Sheet.

|  |  |
| --- | --- |
| (i) |  |

**(1)**

|  |  |
| --- | --- |
| (ii) |  |

**(1)**

|  |  |
| --- | --- |
| (iii) |  |

**(1)**

|  |  |
| --- | --- |
| (iv) |  |

**(1)**

(b)     A simple chemical test can be used to distinguish between cyclohexane (**A**) and cyclohexene (**D**).
Give a reagent for this test and state what you would observe with each compound.

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*(Extra space)* .................................................................................................

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**(3)**

(c)     Cyclohexanol (**B**) can be converted into cyclohexanone (**C**).

Give a reagent or combination of reagents that can be used for this reaction and state the type of reaction.

State the class of alcohols to which cyclohexanol belongs.

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........................................................................................................................

*(Extra space)* .................................................................................................

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**(3)**

(d)     Cyclohexane (**A**) can be converted into bromocyclohexane (**E**) by a reaction that is similar to the reaction of methane either with chlorine or with bromine.

Name and outline a mechanism for the reaction of methane (CH4) with bromine to form bromomethane (CH3Br). Give **one** condition for this reaction to occur.
Write an equation for each step in your mechanism.

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*(Extra space)* .................................................................................................

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**(5)**

**(Total 15 marks)**

**Q34.**When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a)     Compounds **F** and **G** have the molecular formula C6H4N2O4 and both are dinitrobenzenes.
**F** has two peaks in its 13C n.m.r. spectrum.
**G** has three peaks in its 13C n.m.r. spectrum.

**FG**

**(2)**

(b)     Compounds **H** and **J** have the molecular formula C6H12.
Both have only one peak in their 1H n.m.r. spectra.
**H** reacts with aqueous bromine but **J** does not.

**HJ**

**(2)**

(c)     **K** and **L** are cyclic compounds with the molecular formula C6H10O.
Both have four peaks in their 13C n.m.r. spectra.
**K** is a ketone and **L** is an aldehyde.

**KL**

**(2)**

(d)     Compounds **M** and **N** have the molecular formula C6H15N.
**M** is a tertiary amine with only two peaks in its 1H n.m.r. spectrum.
**N** is a secondary amine with only three peaks in its 1H n.m.r. spectrum.

**MN**

**(2)**

**(Total 8 marks)**

**Q35.**When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a)     Compounds **F** and **G** have the molecular formula C6H4N2O4 and both are dinitrobenzenes.
**F** has two peaks in its 13C n.m.r. spectrum.
**G** has three peaks in its 13C n.m.r. spectrum.

**FG**

**(2)**

(b)     Compounds **H** and **J** have the molecular formula C6H12.
Both have only one peak in their 1H n.m.r. spectra.
**H** reacts with aqueous bromine but **J** does not.

**HJ**

**(2)**

(c)     **K** and **L** are cyclic compounds with the molecular formula C6H10O.
Both have four peaks in their 13C n.m.r. spectra.
**K** is a ketone and **L** is an aldehyde.

**KL**

**(2)**

(d)     Compounds **M** and **N** have the molecular formula C6H15N.
**M** is a tertiary amine with only two peaks in its 1H n.m.r. spectrum.
**N** is a secondary amine with only three peaks in its 1H n.m.r. spectrum.

**MN**

**(2)**

**(Total 8 marks)**

**M1.**         (a)     ***R***: O‑H (alcohols) **(1)
*S***: C=O or carbonyl **(1)**

**2**

(b)     aldehyde **(1)** ‑CHO or RCHO **(1)**

**1**

(c)     (i)      *Reason 1*: TMS inert or non-toxic or volatile / easily removed
*Reason 2*: single (intense) peak
               peak of 12 protons
               has 12 equivalent protons
               all protons in same environment
OR
               peak / signal upfield of others
               highly shielded
               more shielded
               peak away from others or δ = 0 or low

*not solvent, not cheap*

*any 2 reasons × (1)*

(ii)     *Solvent*: CDCl3 or CCl4 **(NOT D2O)***Reason*: proton free **(1)**

*allow no hydrogens (atoms)*

*NOT H+ / hydrogen ions*

**4**

(d)     (i)       **(1)**

(ii)     –OH **(1)**

(iii)     –CH2–CH2– **(1)**

**3**

(e)     **(1)**

**1**

**[11]**

**M2.**          (a)      **(1)**

**1**

(b)     *Name of mechanism*: (nucleophilic) addition- elimination **(1)**

*Mechanism*:



**5**

(c)     CH3CH2COOCH2CH3+•→CH3CH2C+=O **(1)** + CH3CH2O•

*equation (1)*

**2**

(d)     CH3CH2CH2COOCH3 or (CH3)2CHCOOCH3 **(1)**

*Allow C3H7COOCH3*

**1**

**[9]**

**M3.**         (a)     2-chloropropanoic acid **(1)**

**1**

(b)     δ 1.72 Doublet  next to CH **(1)**

δ 4.44 Quartet  next to CH3 **(1)**

**2**

(c)     Two triplets **(1)**

**1**

(d)



*Allow SN1*

**5**

(e)     (i)      

(ii)     

(iii)



*Or anhydride*

**3**

**[12]**

**M4.**          (a)     Identity of **X**; 2-methylpropene **(1)**Absorption at 1650 cm–1 indicates an alkene present **(1)**

*OR a chemical answer e.g. Br2 (aq) brown to colourless*

**2**

(b)     Reagents
Step 1 KOH (allow NaOH) **(1)** alcoholic **(1)** warm **(1)**

*Only allow solvent and warm if reagent correct*

Step 2 HBr **(1)**

Mechanism:                    A → **X**

****

*Or a carbocation mechanism*

Mechanism                     **X** → B



**11**

(c)     A gives three peaks **(1)**B gives one peak **(1)**

*Allow one for “A has more peaks than B” when no number of peaks is given*

**2**

**[15]**

**M5.          Part (a)** for each section:

A totally wrong reagent scores zero
An incomplete reagent such as silver nitrate for Tollens, loses the reagent mark, but can get both observation marks.
A wrong reagent such as [Ag(NH3)2]2+ or bromide water loses the reagent mark and the next mark “gained”, i.e. can only score 1/3 if both observations correct

If two tests given and results given correctly for both compounds in both tests then full marks If one test on A and a different test on B with only these results given
if both results correct then score 2/3
if either result wrong then score 1/3
if either test would not work as a distinction, then score 0/3

          If the candidate says A = ketone (or C = benzene), lose this mark.

If the candidate omits the letters when referring to the pair of compounds,
e.g. says alkene decolourises / alkane no reaction penalise one mark only.

(a)     (i)      penalise observations which just say colour change occurs or only state starting colour

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Tollens | [1] | Fehlings / Benedicts | [1] | Brady’s or 2,4-dnph | [1] | sodium | [1] |
| No reaction A | [1] | no reaction A | [1] | no reaction A | [1] | bubbles or hydrogen A | [1] |
| silver mirror or grey or ppt B | [1] | red or ppt B | [1] | (Yellow / orange) Xtals or ppt | [1] | no reaction B | [1] |
| (not silver solution) | [1] | not red solution | [1] | not yellow / orange solution | [1] |   |   |

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Carboxylic acid / H2SO4 | [1] | Schiff’s | [1] | iodoform or I2 / NaOH | [1] | PCl5 | [1] |
| (sweet) smell A | [1] | no reaction A | [1] | yellow (ppt) A | [1] | (misty) fumes A | [1] |
| no reaction B | [1] | goes pink B | [1] | no reaction B | [1] | no reaction B | [1] |

(ii)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Bromine (water) | [1] | KMnO4 | [1] | KMnO4 / H2SO4 | [1] |   | [1] |
| no reaction C | [1] | no reaction C | [1] | no reaction C | [1] |   | [1] |
| decolourised D | [1] | goes brown D | [1] | goes colourless D | [1] |   | [1] |
| not clear not discolour (is)ed |   |   |   |   |   |   |   |

(iii)     not just smell for E

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| an identified (hydrogen) carbonate | [1] | correct metal | [1] | UI or stated indicator | [1] | PCl5 | [1] |
| no reaction E | [1] | no reaction E | [1] | no change E | [1] | (misty) fumes E | [1] |
| bubbles or CO2 F | [1] | bubbles or H2 F | [1] | red or correct colour F | [1] | no reaction F | [1] |

**note MAX 8**

(b)     F has absorption at 2500 – 3000 cm–1 (due to COOH) **(1)
N.B.** Qu asks “How fingerprinting is used” i.e. no marks for simply
stating fingerprint region unique.
Compare with (spectrum of) known compound or database **(1)**(exact) match

**3**

(c)     major peak [CH3CO]+ **(1)**m / z           43 **(1)**CH3COOCH3+**.** → CH3CO++ OCH3**.**

*(1 for molecular ion)     (1 for correct other fragment)*

**Alternative:**

          major peak [CH3]+ **(1)**m /z         15 **(1)**CH3COOCH3+**.** → CH3++ CH3COO**.** or COOCH3**.** or C2H3O2**.** or C3H6O2+**.**

*(1)   (1 for radical)*

          If major peak wrong but possible e.g. CH3OO+ m/z = 59
no marks so far, but can score up to 2 for
CH3COOCH3+**.** → CH3COO+ or +COOCH3 + CH3

*1 for correct other fragment]*

**4**

**[15]**

**M6.**          (a)     5 **(1)**

**1**

(b)     2:2:2:3:3 **(1)**

*any order but not multiples*

**1**

(c)      **(1)**

**1**

(d)     CH3CH2 or C2H5 or ethyl **(1)**δ4.13 (quartet) : CH2 peak split by CH3 / next to CH3 **(1)**δ1.26 (triplet) : CH3 peak split by CH2 / next to CH2 **(1)**

**3**

(e)     CH2CH2 **(1)**

**1**

(f)      **(2)**

*allow* ***(1)*** *for CH3COCH2CH*2OCOCH2CH3

*or CH3COOCH2CH*2COCH2CH3

*Must be C7H12O3*

**2**

**[9]**

**M7.**          (a)     X contains > C=O **(1)**

*if X and Y reversed lose this mark but allow remaining max 6/7*

** X is CH3CH2COOH **(1)**

**** Y is CH3CH2CH2OH **(1)**

**** A is  **(1)**

****

Conc H2SO4 : catalyst **(1)**

**7**

(b)



**4**

(c)             3.1 – 3.9 **(1)**

****   2.1 – 2.6 **(1)**

a: quartet **(1)**  3 adjacent H **(1)**

b: triplet **(1)**  2 adjacent H **(1)**

**6**

(d)     3269 cm–1 OH  alcohol **(1)**

**** G is  (1)

**2**

          **Notes**

(a)     first mark for C=O stated or shown in **X**

*Ignore wrong names*

          **Y** CH3CH2CH2OH
allow C3H7 in **A** if **Y** correct or vice versa
Allow **(1)** for **A** if correct conseq to wrong **X** and **Y**

          other oxidising agents: acidified KMnO4; Tollens; Fehlings

          other reducing agents: LiAlH4; Na/ethanol; Ni/H2; Zn or Sn or Fe/HCl

(b)     give **(1)** for carboxylic acid stated or COOH shown in each suggestion
**(1)** for correct **E**any 2 out of 3 for **B**, **C** or **D**allow C3H7 for either the **B** or **D** shown on the mark scheme
i.e. a correct structure labelled **B**, **C** or **D** or **E** will gain 2.

(c)     protons a – *quartet* must be correct to score *3 adjacent H* mark. Same for b

(d)     allow **(1)** for any OH (alcohol) shown correctly in any structure – ignore extra functional groups. Structure must be completely correct to gain second mark

**[19]**

          Organic points

(1)     Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2)     Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

          allow CH3– or –CH3 or  or CH3    or   H3C–

**M8.**          (a)     C=O **(1)**

*or “carbonyl”*

**1**

(b)     (i)      Cl has (2) isotopes **(1)**

*Allow 35Cl and 37Cl without word isotope – but must be correct isotopes*

*must have 3 different elements, i.e. not C3H7+ but allow balanced equation including C3H7+ for the equation mark*

(ii)     *Fragmentation*:  **(1)**

*must be an ion (\*)*

*Equation*: C4H7ClO+• →  + C2H4Cl• **(1)**

*(\*) allow C2H3O+ or any form of it (i.e. CH2CHO+ or CH2COH+) in equation, be generous with position of + or •*

*if fragment ion completely wrong (not m/z = 43) no further marks*

**3**

(c)     (i)      CDCl3 or CCl4 **(1)** or D2O, C6D6

(ii)     Si(CH3)4 **(1)** or SiC4H12

**2**

(d)     **(1)**

|  |  |  |  |
| --- | --- | --- | --- |
|   | Peak 1 | Peak 2 | Peak  |
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |
| Number of adjacent, non-equivalent protons | 1 | **0** | **3** |

**1**

(e)      **(1)**

or CH3COCHClCH3

**1**

(f)

           **(1)**

**1**

**[9]**

**M9.**          **X** is methyl propanoate



**1**

          M1 for arrow and lone pair,

**4**

M2 for arrow
addition-elimination

**1**

          Spectrum 2

*if thinks Spectrum 1 = X can only score for structure of Y*

**1**

**Y** is CH3COOCH2CH3

**1**

The two marks for explanation are awarded for discussing one or more of the
four peaks (not those for the CH3 of the ethyl groups)
for stated δ values the integration or the splitting should be related to the
structure: e.g. structure of **X** shows that
at δ 3.7 – 4.1 **(1)** spectrum of **X** should have integration 3 / singlet **(1)**

or

at δ 2.1 – 2.6 **(1)** spectrum of **X** should have integration 2 / quartet **(1)**

Spectrum 2 has these
[OR Spectrum 1 has
at 3.7 – 4.1 **(1)** quartet / integration 2 **(1)** so not **X**at 2.1 – 2.6 **(1)** singlet / integration 3 **(1)** so not **X**]

**2**

**[10]**

**M10.**          (a)     Pentan-2-one

**1**

(b)     (i)      1680 – 1750 (cm–1)

**1**

(ii)     3230 – 3550 or 1000 – 1300 (cm–1)

**1**

(iii)     4

**1**

(c)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Reagent | K2Cr2O7/H+ | KMnO4 /H+ | Na | CH3COOH/H2SO4 | **1** |
| with **C** | no reaction | no reaction | no reaction | no reaction | **1** |
| with **D** | goes green | goes colourless | effervescence | smell | **1** |

*(penalise incomplete reagent e.g. K2Cr2O7 or Cr2O7 2–/H+ then mark on)*

(d)

|  |  |  |  |
| --- | --- | --- | --- |
| Reagent | Tollens | Fehlings or Benedicts | **1** |
| with **E** | silver(mirror) | red ppt or goes red*(not red solution)* | **1** |
|   |   |   |   |

**[9]**

**M11.**         (a)     (i)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Reagent | Tollens | Fehlings or Benedicts | K2Cr2O7/H+or acidified | KMnO4/H+ | I2/NaOH |
| Propanal | silver (mirror) | red ppt or goes red*(not red solution)* | goes green | goes colourless | Noreaction |
| Propanone | no reaction | no reaction | no reaction | no reaction | Yellow(ppt) |

*(penalise incomplete reagent e.g. K*2*Cr*2*O*7 *or Cr*2*O*72–*/H*+ *then mark on)*

**3**

(ii)     propanal 3 peaks

*ignore splitting even if wrong*

**1**

propanone 1 peak

**1**

(b)     **X** is CH3CH2COOH or propanoic acid  if both name and formula given,
                                                             both must be correct, but

**1**

          **Y** is CH3CH(OH)CH3 or propan-2-ol     allow propanol with correct formula

**1**

**Mark the type of reaction and reagent/condition independently.
The reagent must be correct or close to score condition**

Step 1        Oxidation

         K2Cr2O7/H+ or other oxidation methods as above
allow Cr2O72–H+ if penalised above (ecf)
reflux (not Tollens/Fehlings) or heat or warm

**1**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Step 2 | reduction or nucleophilicaddition | reduction ornucleophilic addition | reduction or hydrogenation | **1** |
|   | NaBH4 | LiAlH4 | H2 | **1** |
|   | in (m)ethanol or water or etheror dry | ether or dry | Ni / Pt etc | **1** |

Step 3        esterification or (nucleophilic) addition-elimination or condensation

**1**

(conc) H2SO4 or HCl

**1**

warm (allow without acid reagent if **X** and **Y** given as reagents)

**1**

or reflux or heat

**1**

**[15]**

**M12.**          (a)     butanoyl chloride

**1**

(b)     (i)      Cl has (two) isotopes or 35Cl and 37C1

**1**

(ii)     106 **and** 108

**1**

(c)     (nucleophilic) addition-elimination, penalise electrophilic
not esterification



**1**

M3 for structure
M4 for 3 arrows and lone pair
(only allow for correct M3 or close)

M2 not allowed independent of M1,
but allow M1 for correct attack on C+ if M2 shown as independent first.

**4**

**[8]**

**M13.**         (a)     **A**       any C5 alkene

**1**

**B**

****

**1**

(b)     **C**

****

         or CH3COOH    or      HCOOCH3

**1**

          **D**

****

         or HOCH2CHO

**1**

(c)     **E**

****

**1**

          **F**

****

**1**

(d)     **G**

****

**1**

          **H**

****

**1**

(e)     **I**

****

**1**

          **J**

****   **NOT** hex-3-ene

**1**

**[10]**

**M14.**          (a)     (i)

 or RCOCH3;

*(or description in words)
(ignore trailing bonds)*

**1**

(ii)     H3C—O or ROCH3;

*(allow 1 if both (i) and (ii) give CH3- or H3C– only)*

**1**

(iii)     CH2CH2 or two adjacent methylene groups;

**1**

(iv)



*OR*

CH3COCH2CH2OCH3;

**1**

(b)     (i)      OH in acids or (carboxylic) acid present

(ii)



(c)

|  |  |  |
| --- | --- | --- |
| reagent | K2Cr2O7 /H+ | KMnO4 /H+ |
| **Y** | no reaction | no reaction |
| **Z** | orange to green or turns green | purple to colourlessor turns colourless |

**5**

**[9]**

**M15.**          (a)     (i)      3 peaks or shown in a list

**1**

*m/z* = 126, 128 and 130 (56 +70/72/74)

*(all 3 scores 2)*

*(if 56 wrong allow (x + 70/72/74) for 1(x cannot be zero)*

*(any two scores 1)*

**2**

(ii)


(1)                                           (1)                                 (1)

allow wrong structure                    for structure                  dot can be
                                                                                   anywhere

**3**

(b)     (i)      optical

**1**

equal mixture of enantiomers

**1**

(optically) inactive or effects cancel

**1**

plane polarised light                    use stereospecific reagent (QoL)

**1**

rotated in opposite/different

directions (QoL)                          reacts with one isomer only

**1**

(ii)     carbocation

**1**

planar

*(must refer to carbocation or intermediate)*

**1**

attack from either side equally likely

*(must refer to carbocation /intermediate)*

**1**

**7 max**

(c)     (i)      2 peaks

*(if 4 peaks allow splitting only)*

**1**

ratio 6:2 or 3:1

**1**

doublet (6 or 3)

**1**

quartet (2 or 1)

**1**

(ii)     **S**

          

**1**

**T**

          

**1**

**[19]**

**M16.**          (a)     **X** (O–H) (alcohols)

*penalise acid or missing “alcohol”*

**1**

**Y** C=O

*allow carbonyl*

**1**

****

*NOT acid*

**4**

(b)



*Allow conseq dibromocompounds following incorrect unbranched alkenes*

*NOT allow dibromocompound consequent on a duplicate alkene*

*NOT allow monobromocompounds if HBr added*

**3**

****

**3**

6:3:1 either next to correct structure or to none

**1**

Allow a mark for identifying correct dibromocompound with three peaks
even if integration ratio is wrong

**1**

if 6:3:1 missing or wrong, no marks for splitting

Only award a mark for splitting if it is clear which integration number it
refers to

6 singlet or drawn

**1**

3 doublet or drawn

**1**

1 quartet/quadruplet or drawn

**1**

**(max 10 marks)**

**[16]**

**M17.**          (a)     (i)      There are three pairs of equivalent carbon atoms

**1**

(ii)     75ppm

**1**

(b)     (i)      4

**1**

(ii)     2

**1**

(c)     Each structure can represent a pair of cis/Z and trans/E isomers
OR
Optical isomers

**1**

**[5]**

**M18.**          (a)     GLC or distillation

**1**

(b)     C=O

**1**

(c)     (i)      Cl has two isotopes

**1**

(ii)     

**1**

C4H7ClO+• →  + C2H4Cl•

**1**

(d)     (i)      e.g. CDCl3 or CCl4

**1**

(ii)     Si(CH3)4

**1**

(e)     0 and 3

**1**

(f)



**1**

(g)     CH3CH2CH2COCl or (CH3)2CHCOCl

**1**

**[10]**

**M19.**          (a)     Allow 1 mark each for any correctly drawn primary, secondary and
tertiary alcohol of molecular formula C4H8O

**3**

          Tertiary alcohol cannot be oxidised

**1**

(b)     Region 1500–400 cm–1

**1**

exact match to spectrum of known compound

**1**

(c)                       **A**                                               **B**       CH3CH2CH2OH                       CH3CH2–O–CH3 **(1)**or CH3CH(OH)CH3 **(1)**

                           **C**                                               **D**       one alkene e.g.                     one cycloalkane e.g.

|  |  |
| --- | --- |
| CH2=CHCH2CH2CH3CH3–CH=CH–CH2CH3(CH3)2C=CHCH3H2C=C(CH3)CH2CH3 | **(1)** etc |

                           **E**                                                **F**      CH3CH2CHO **(1)**                         CH3COCH3 **(1)**

**6**

**[12]**

**M20.**          (a)     Secondary ***OR***2° (alcohol);

**1**

(b)     Spectrum is for **butanone (or formula) or butan-2-one**

*The explanation marks depend on correctly identifying butanone.*

          If butanone is correctly identified, award any two from

•        (Strong) absorption / peak at approximately 1700 (cm–1) /
1710 (cm–1) / in the range 1680 – 1750 (cm–1) This
needs to be stated.

•        (Characteristic) absorption / peak for C=O (may be shown
on the spectrum in the correct place).

•        No absorption / peak in range 3230 to 3550 cm–1.

**1**

•        No absorption / peak for an OH group.

*Look at the spectrum to see if anything is written on it that might gain credit.
Allow the words “dip” OR “spike” OR “low transmittance” as alternatives for absorption.*

**2**

(c)     Displayed structure for 2-methylpropan-2-ol


*Must have* ***all bonds*** *drawn out but ignore the bond angles*

**1**

**[5]**

**M21.**          (a)     A



*allow CH3COCH3*

**1**

          B       

*must show C=C*

*Penalise sticks once per pair*

**1**

(b)     C       CH3CH2CH2CH2CH3

**1**

D       

*NOT cyclopentane which is only C5H****10***

*Penalise sticks once per pair*

**1**

(c)     E       CH3CH2COOCH3

*Allow C2H5CO2CH3*

**1**

F       CH3COOCH2CH3

*Allow CH3CO2CH2CH3 or CH3CO2C2H5Penalise sticks once per pair*

**1**

(d)     G       

         allow C3H7                           allow C3H7                                allow C2H5

*not C5H11 nor C4H9*

*Penalise sticks once per pair*

**1**

H       

allow C2H5

**1**

(e)     I         

allow C2H5

**1**

J        

*NOT C3H7Penalise sticks once per pair*

**1**

**[10]**

##

          (a)     Average/mean mass of (1) atom(s) (of an element)
1/12 mass of one atom of 12C

**1**

*If moles and atoms mixes Max = 1*

**1**

***OR***

(Average) mass of one mole of atoms
1/12 mass of one mole of 12C

***OR***

(Weighted) average mass of all the isotopes
1/12 mass of one atom of 12C

***OR***

Average mass of an atom/isotope compared to C-12 on a scale in
which an atom of C-12 has a mass of 12

*This expression = 2 marks*

(b)     d block

*Allow 3d/D
Other numbers lose M1
Ignore transition metals*

**1**

[Ar] 3d24s2

**1**

*Can be written in full
Allow subscripts
3d2 and 4s2 can be in either order*

27

**1**

(c)     

(= 1550)

**1**

(or ∑ their abundances)

*If one graph reading error lose M1 and allow consequential M2 and M3.
If 2 GR errors penalise M1 and M2 but allow consequential M3
If not 17 or ∑ their abundances lose M2 and M3*

**1**

= 91.2

*91.2 = 3 marks provided working shown.*

**1**

Zr/Zirconium

*M4 -allow nearest consequential element from M3
accept Zr in any circumstance*

**1**

(d)     High energy electrons/bombarded or hit with electrons

*accept electron gun*

**1**

knocks out electron(s) (to form ions)

**1**

Z+ = 90 deflected most

*If not 90 lose M3 and M4
If charge is wrong on 90 isotope lose M3 only
Accept any symbol in place of Z*

**1**

since lowest mass/lowest m/z

*Allow lightest*

**1**

(e)     (ions hit detector and) cause current/(ions) accept electrons/cause
electron flow

*QWC*

**1**

bigger current = more of that isotope/current proportional to abundance

*Implication that current depends on the number of ions*

**1**

**[15]**

**M23.**          (a)     chromatography (allow GLC TLC GC HPLC)

*allow any qualification*

**1**

(b)     5

**1**

Allow 320(.0) or 322(.0)

**1**

(c)     Use of excess air/oxygen or high temperature (over 800 °C)
or remove chlorine-containing compounds before incineration

**1**

(d)     (i)      Si(CH3)4 allow SiC4H12

*allow displayed formula and do not penalise sticks*

*Not TMS*

**1**

(ii)     3

**1**

**[6]**

**M24.**          (a)     (i)



*not allow C3H7*

*allow C2H5 bonded to C either way round*

**1**

(ii)     elimination

*allow base – elimination*

*but penalise any other qualification*

**1**

(iii)     Z-pent-2-ene or cis-pent-2-ene               either Z or cis is necessary
(allow Z-2-pentene or cis-2-pentene)

*with or without brackets around Z
with or without hyphens*

**1**

(b)     (i)      C

**1**

(ii)     A

**1**

(iii)     B

**1**

(iv)    D

**1**

(c)



*allow C2H5 bonded via C or H*

*must have both trailing bonds
ignore brackets or n*

**1**

addition or radical or step or chain growth

*QOL not additional*

**1**

(d)     (i)



*Allow SN1, i.e M2 first then attack of NH3 on carbocation.*

*Allow C2H5 in M3 bonded either way*

*Allow with or without NH3 to remove H+ in M4, but lose mark if Br– used.*

*ignore δ+ or δ– unless wrong*

*+ on central C instead of δ + loses M2*

**4**

(ii)     excess NH3

*ignore reflux*

*allow conc ammonia in sealed tube*

**1**

(iii)



*Allow C2H5 bonded either way*

**1**

(e)     (i)



**1**

(ii)



*NOT (C2H5)2NCH3 which is tertiary with 3 peaks but its spectrum has no doublet.*

**1**

**[17]**

**M25.**          (a)     **J** (acid) amide

*not peptide, not N-substituted amide*

**1**

**K** (secondary) amine or amino

*penalise primary or tertiary
allow N-substituted amine*

**1**

(b)     (δ =) 3.1-3.9

**1**

doublet **OR** duplet

*Not 3.7 – 4.1*

*Not secondary
name required not the number 2*

**1**

(c)     (i)      Solvent must be proton-free

**OR** CHCl3 has protons or has H or gives a peak

**1**

(ii)     CDCl3 is polar **OR** CCl4 is non-polar

**1**

(d)     11 **OR** eleven

**1**

(e)     (i)      Si(CH3)4 **OR** SiC4H12

*ignore TMS*

**1**

(ii)     a single number or a range within 21-25

*penalise anything outside this range*

**1**

(iii)



*allow ring around the C only and also allow*

**

**1**

(f)      (i)      NaBH4

*ignore name if formula correct*

*ignore solvent*

*allow LiAlH4   Zn/HCl   Sn/HCl   H2/Ni   H2/Pt*

**1**

(ii)



*allow ring around the C only*

**1**

(iii)     (plane) polarised light **OR** light in a polarimeter

**1**

polarised light is not rotated or is unaffected

*penalise bent/diffracted/deflected/reflected*

*Not just solution is optically inactive*

**1**

(iv)    **adv** cheaper medicine due to cost or difficulty of separation or
both can lower blood pressure

**OR** more effective/beneficial with a reason

*or no need to separate*

**1**

**disadv** may be side effects from one enantiomer in the mixture or
only half the product works or one enantiomer may be
ineffective or double dose required

**1**

**[16]**

**M26.**          (a)     (i)      Single reagent

If wrong single reagent, CE = zero

Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.NaCO3) loses reagent mark, but mark on

For “no reaction” allow “nothing”

Different reagents

If different tests on E and F; both reagents and any follow
on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.
i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

PCl5 PCl3

SOCl2

**1**

**E** ester

Na2CO3/NaHCO3 named carbonate

metal e.g.Mg

no reaction

no reaction

named indicator

no effect

No reaction

**1**

**F** acid

Na2CO3/NaHCO3 named carbonate

Effervescence or CO2

metal e.g.Mg

Effervescence or H2

named indicator

acid colour

*fumes*

**1**

(ii)     Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong
formula (e.g.NaCO3) loses reagent mark, but mark on
**For “no reaction” allow “nothing”**

Different reagents

If different tests on E and F; **both** reagents and any
follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on
G (ketone) – no reaction.
Second and third marks are for correct observations.

**1**

**i.e. for different tests on E and F, if one reagent is correct
and one wrong, can score max 1 for correct observation
with correct reagent.**

**G** ketone

AgNO3

no reaction

Na2CO3/NaHCO3 named carbonate

water

no reaction

named indicator

no effect

Named alcohol

no reaction

Named amine or ammonia

no reaction

**1**

**H** Acyl chloride

AgNO3

(white) ppt

Na2CO3/NaHCO3 named carbonate

Effervescence or CO2 or fumes or exothermic

water

fumes

named indicator

acid colour

Named alcohol

Smell or fumes

Named amine or ammonia

fumes

**1**

*Allow iodoform test or Brady’s reagent (2,4,dnph) test (both positive for G)*

(iii)     Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong
formula (e.g.NaCO3) loses reagent mark, but mark on

For “no reaction” allow “nothing”

Different reagents

If different tests on E and F; **both** reagents and any follow
on chemistry must be correct for first (reagent) mark.

Reagent must react: i.e. not allow Tollens on
G (ketone) – no reaction.

Second and third marks are for correct observations.

i.e. for different tests on E and F, if one reagent is correct
and one wrong, can score max 1 for correct observation
with correct reagent.

**1**

**J** Primary alcohol

K2Cr2O7/ H+

goes green

KMnO4/ H+

decolourised / goes brown

Lucas test (ZnCl2/HCl)

*Penalise missing H+ but mark on*

**1**

**K** Tertiary alcohol

K2Cr2O7/ H+

No reaction

KMnO4/ H+

no reaction

Lucas test (ZnCl2/HCl)

Rapid cloudiness

**1**

*If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation*

(b)     (i)      3,3-dimethylbutan-1-ol

*Allow 3,3-dimethyl-1-butanol*

**1**

4

**1**

Triplet on three

**1**

(ii)     2-methylpentan-2-ol

*Allow 2-methyl-2-pentanol*

**1**

5

**1**

Singlet or one or no splitting

**1**

**[15]**

**M27.**          (a)     Benzene-1,2-dicarboxylic acid

*Allow 1,2-benzenedicarboxylic acid*

**1**

(b)



*Must show all bonds including trailing bonds*

*Ignore n*

**1**

(c)     (i)      2 C2H5OH

*NB Two ethanols*

**1**

H2O

*but only one water*

**1**

(ii)     6 or six

**1**

(iii)



*Ignore overlap with O to the left or H to the*

*right, but must only include this one carbon.*

*either or allow both (as they are identical)*

**1**

(d)



*Allow + on C or O in *

**1**

*Dot must be on O in radical*

**1**

(e)     (i)      Rate = *k*[DEP]

*Must have brackets but can be ( )*

**1**

(ii)     Any **two** of

•        experiment repeated/continued over a long period

•        repeated by independent body/other scientists/avoiding
bias

•        investigate breakdown products

•        results made public

*Not just repetition*

*Ignore animal testing*

**2 max**

**[11]**

**M28.**          (a)     Pentan-2-one

*ONLY but ignore absence of hyphens*

**1**

(b)     Functional group (isomerism)

*Both words needed*

**1**

(c)     (i)



*Award credit provided it is obvious that the candidate is drawing the Z / cis isomer*

*The group needs to be CHOHCH3 but do not penalise poor C–C bonds or absence of brackets around OH*

*Trigonal planar structure not essential*

**1**

(ii)     Restricted rotation (about the C=C)

OR

No (free) rotation (about the C=C)

**1**

(d)

|  |  |
| --- | --- |
| **M1** Tollens’ (reagent)*(Credit ammoniacal silver nitrate OR a description of making Tollens’)**(Do not credit Ag+, AgNO3 or [Ag(NH3)2+] or “the silver mirror test” on their own, butmark M2 and M3)* | **M1** Fehling’s (solution) / Benedict’s*(Penalise Cu2+(aq) or CuSO4 but mark M2 and M3)* |
| **M2** silver mirrorOR black solid or black precipitate | **M2** Red solid/precipitate*(Credit orange or brown solid)* |
| **M3** (stays) colourlessORno (observed) change / no reaction | **M3** (stays) blueORno (observed) change / no reaction |

*If* ***M1*** *is blank CE = 0, for the clip*

*Check the partial reagents listed and if M1 has a totally incorrect reagent, CE = 0 for the clip*

*Allow the following alternatives*

***M1*** *(acidified) potassium dichromate(VI) (solution); mark on from incomplete formulae or incorrect oxidation state*

***M2*** *(turns) green*

*M3 (stays) orange / no (observed) change / no reaction*

*OR*

***M1*** *(acidified) potassium manganate(VII) (solution);*

*mark on from incomplete formulae or incorrect oxidation state*

***M2*** *(turns) colourless*

***M3*** *(stays) purple / no (observed) change / no reaction*

*In all cases for* ***M3***

*Ignore “nothing (happens)”*

*Ignore “no observation”*

**3**

(e)     (i)      **Spectrum is for Isomer 1**

or named or correctly identified

*The explanation marks in (e)(ii) depend on correctly identifying Isomer 1.*

*The identification should be unambiguous but candidates should not be penalised for an imperfect or incomplete name. They may say “the alcohol” or the “alkene” or the “E isomer”*

**1**

(ii)     **If Isomer 1 is correctly identified, award any two from**

•        (Strong / broad) absorption / peak in the range
**3230 to 3550** cm–1 or specified value in this range
or **marked correctly** on spectrum
**and**(characteristic absorption / peak for) OH group /**alcohol** group

•        No absorption / peak in range **1680 to 1750** cm–1 or
absence marked correctly on spectrum
**and**(No absorption / peak for a) **C=O** group / **carbonyl** group / **carbon-oxygen double bond**

•        Absorption / peak in the range **1620 to 1680** cm–1or specified value in this range or marked correctly
on spectrum
**and**

          (characteristic absorption / peak for) **C=C** group
/ **alkene** / **carbon-carbon double bond**

*If 6(e)(i) is incorrect or blank, CE=0*

*Allow the words “dip” OR “spike” OR “trough” OR “low transmittance” as alternatives for absorption.*

*Ignore reference to other absorptions e.g. C-H, C-O*

**2**

**[10]**

**M29.**          (a)     (i)      Different number / amount of neutrons

*Not different neutrons*

*Ignore same protons and/or electrons*

*CE incorrect statement relating to protons / electrons*

**1**

(ii)     Same electron configuration / same number of
electrons (in the outer shell)

*Ignore same no of protons*

*Ignore electrons determine chemical properties*

*CE if wrong statement relating to protons / neutrons*

**1**

(b)     Average mass of 1 atom (of an element)
1/12 mass atom of 12C

OR

Average/mean mass of atoms of an element
1/12 mass of one atom of 12C

OR

(Average) mass of one mole of atoms
1/12 mass of one mole of 12C

OR

(Weighted) average mass of all the isotopes
1/12 mass of one atom of 12C

OR

Average mass of an atom/isotope compared to C-12
on a scale in which an atom of C-12 has a mass of 12

*If moles and atoms mixes Max = 1*

*Mark top and bottom line independently*

*1/12 on bottom line can be represented as x 12 on top line*

*This expression = 2 marks*

**2**

(c)     (i)      

= 65.6

*If not 27 max 1 mark (for top line)*

*Mark is for dividing by 27 or string*

*If* ***evidence*** *of arithmetic or transcription error seen in M1 or M2 allow consequential M3 and consequential (c)(ii)*

*65.6 = 3 marks*

**3**

(ii)     64Zn+

*M1 for identifying Zn / zinc*

*M2 is for the + sign and the 64*

*M2 is dependent on M1*

**2**

(d)     Size of the charge (on the ion) / different charges / different m/z

*Allow forms 2+ ions*

*QWC*

**1**

(e)     (ions hit detector and) cause current/(ions) accept
electrons/cause electron flow/electric pulse caused
bigger current = more of that isotope/current proportional to abundance

*Implication that current depends on the number of ions*

*M2 dependent on M1*

**2**

**[12]**

**M30.**(a)      (i)     Conc HNO3

*If either or both conc missing, allow one;*

**1**

Conc H2SO4

*this one mark can be gained in equation`*

**1**

2 H2SO4 + HNO3  2 HSO4– + NO2+ + H3O+

**1**

***OR***     H2SO4 + HNO3  HSO4– + NO2+ + H2O

*Allow + anywhere on NO2+*

***OR***     via two equations

           H2SO4 + HNO3  HSO4– + H2NO3+

           H2NO3+  NO2+ + H2O

(ii)

*•   ignore position or absence of methyl group in M1 but must be in     correct position for M2*

*•   M1 arrow from within hexagon to N or + on N*

*•  Allow NO2+ in mechanism*

*•   Bond to NO2 must be to N*

*•   horseshoe must not extend beyond C2 to C6 but can be smaller*

*•   + not too close to C1*

*•   M3 arrow into hexagon unless Kekule*

*•   allow M3 arrow independent of M2 structure*

*•   ignore base removing H in M3*

*•   + on H in intermediate loses M2 not M3*

**3**

(b)     5

**1**

(c)     2

**1**

(d)     2C7H5N3O6      5H2O   +   3N2   +   7C   +   7CO

*Or halved*

**1**

**[9]**

**M31.**(a)    OH alcohols

**1**

(b)     (i)     2.6



Ignore any group on RHS

*Must clearly indicate relevant* ***two*** *H on a C next to C=O*

On LHS, penalise H or CH or CH2 or CH3

*Ignore missing trailing bonds or attached R groups*

**1**

(ii)     2.2



Ignore all groups on RHS

*Must clearly indicate relevant* ***three*** *H on C next to C=O*

*Ignore missing trailing bonds or attached R group*

**1**

(iii)    1.2



Or in words: two equivalent CH3 groups

*Must clearly indicate two equivalent methyl groups.*

Penalise attached H

*Ignore missing trailing bonds or attached R groups*

**1**

(iv)

**1**

**[5]**

**M32.**(a)    H   ***OR***   hydrogen   ***OR***   H•

*Ignore brackets ignore dot*

*penalise + or – charge*

**1**

(b)     CH3   ***OR***   methyl   ***OR***   CH3•   ***OR***   •CH3

*Ignore brackets ignore dot*

*penalise + or – charge*

**1**

(c)     Either order

C2H5   ***OR***   ethyl   ***OR***   CH3CH2•   ***OR***   C2H5•

*Ignore brackets ignore dot*

*penalise + or – charge*

**1**

CHO   ***OR***   HCO   ***OR***   COH   ***OR***   H—C=O

**1**

(d)     I   A

**1**

II   C

**1**

III   D

**1**

IV   B

**1**

**[8]**

**M33.**(a)     (i)      C

**1**

(ii)     A

**1**

(iii)    D

**1**

(iv)     B

**1**

(b)     **M1** Br2 ***OR*** bromine (water) ***OR*** bromine (in CCl4 / organic solvent)

*If M1, has no reagent or an incorrect reagent, CE=0*

*Ignore “acidified”*

*For M1 penalise Br (or incorrect formula of other correct reagent), but mark on*

*For M1, it must be a whole reagent and/or correct formulae*

**Either order**

*If oxidation state given in name, it must be correct.*

**M2**   cyclohexane ***OR*** **A** or the alkane: remains orange / red / yellow / brown /
the same ***OR*** no reaction ***OR*** reference to colour going to cyclohexane layer

*For M2 credit “no change”*

*Ignore “nothing”*

*Ignore “nothing happens”*

*Ignore “no observation”*

**M3**   cyclohexene ***OR*** **D** or the alkene: decolourised / goes colourless / loses
its colour

*For M3, ignore “goes clear”*

**Alternatives** : potassium manganate(VII)

**M1** KMnO4 in acid **M2** purple **M3** colourless

**M1** KMnO4 in alkali / neutral **M2** purple **M3** brown solid

Give appropriate credit for the use of iodine and observations

*No credit for combustion observations*

**3**

(c)     **M1**   acidified potassium or sodium dichromate

*For M1, it must be a whole reagent and/or correct formulae*

***OR***   eg H2SO4 / K2Cr2O7 ***OR*** H+/ K2Cr2O7

***OR***   correct combination of formula and name

*If oxidation state given in name, it must be correct.*

**M2** oxidation ***OR*** oxidised ***OR*** redox

*Do not penalise incorrect attempt at formula if name is correct or vice versa*

**M3**   secondary / 2o (alcohol)

*Credit acidified potassium chromate(VI) / H2SO4 + K2CrO4*

**3**

(d)     **M1**   (free-) radical substitution (mechanism)

*M1 both words required*

**M2**   Br2      2Br•

*Penalise absence of dot once only.*

**M3**   Br• + CH4      •CH3 + HBr

*Penalise + or – charges every time*

**M4**   Br2 + •CH3      CH3Br + Br•

*Accept dot anywhere on methyl radical*

*Accept a correct termination step for 1 mark if neither M3 nor M4 are scored; otherwise ignore termination steps*

*Mark independently*

*NB If Cl2 is used, penalise every time ( this may be for M2, M3 and M4)*

*If cyclohexane is used, penalise every time (this may be for M3 and M4)*

**M5   Condition**

        ultra-violet / uv / sun light

***OR***   high temperature

***OR***   125 °C ≤ T ≤ 600 °C

***OR***   400 K ≤ T ≤ 870 K

*For M5 ignore “heat”*

**5**

**[15]**

|  |  |
| --- | --- |
| **M34.**(a)     **F** | **G** |
|  |  |

*Penalize –O2N once*

*Penalise missing circle once*

*Don’t penalise attempt at bonding in NO2*

**1**

**1**

|  |  |
| --- | --- |
| (b)     **H** | **J** |
|  |  |

*If* ***both H*** *and* ***J*** *correct but reversed, award one mark*

**1**

**1**

A carbon in saturated ring structures should be shown as



|  |  |
| --- | --- |
| (c)     **K** | **L** |
|  |  |

**1**

**1**

|  |  |
| --- | --- |
| (d)     **M** | **N** |
|  |  |

*Allow C2H5 but*

*NOT allow C4H9 or C3H7*

**1**

**1**

**[8]**

|  |  |
| --- | --- |
| **M35.**(a)     **F** | **G** |
|  |  |

*Penalize –O2N once*

*Penalise missing circle once*

*Don’t penalise attempt at bonding in NO2*

**1**

**1**

|  |  |
| --- | --- |
| (b)     **H** | **J** |
|  |  |

*If* ***both H*** *and* ***J*** *correct but reversed, award one mark*

**1**

**1**

A carbon in saturated ring structures should be shown as



|  |  |
| --- | --- |
| (c)     **K** | **L** |
|  |  |

**1**

**1**

|  |  |
| --- | --- |
| (d)     **M** | **N** |
|  |  |

*Allow C2H5 but*

*NOT allow C4H9 or C3H7*

**1**

**1**

**[8]**