Q12.

Which compound is formed when 1-phenylethanol reacts with acidified potassium dichromate(VI)?

A $C_6H_5CH_2CH_2OH$ ⬭

B $C_6H_5CH_2CHO$ ⬭

C $C_6H_5COCH_3$ ⬭

D $C_6H_5CH_2COOH$ ⬭

(Total 1 mark)

Q13.

The oxidation of propan-1-ol can form propanal and propanoic acid.
The boiling points of these compounds are shown in the table.

Compound	Boiling point / °C
propan-1-ol	97
propanal	49
propanoic acid	141

In a preparation of propanal, propan-1-ol is added dropwise to the oxidising agent and the aldehyde is separated from the reaction mixture by distillation.

(a) Explain, with reference to intermolecular forces, why distillation allows propanal to be separated from the other organic compounds in this reaction mixture.

(3)

(b) Give **two** ways of maximising the yield of propanal obtained by distillation of the reaction mixture.

1.

2.

(2)

(c) Describe how you would carry out a simple test-tube reaction to confirm that the sample of propanal obtained by distillation does **not** contain any propanoic acid.

(2)

(d) A student carried out an experiment to determine the enthalpy of combustion of ethanol. Combustion of 457 mg of ethanol increased the temperature of 150 g of water from 25.1 °C to 40.2 °C

Calculate a value, in kJ mol^{-1}, for the enthalpy of combustion of ethanol in this experiment.
Give your answer to the appropriate number of significant figures.

(The specific heat capacity of water is 4.18 J K^{-1} g^{-1})

Enthalpy of combustion _____ kJ mol^{-1}

(3)

(e) A mixture of isomeric alkenes is produced when pentan-2-ol is dehydrated in the presence of hot concentrated sulfuric acid. Pent-1-ene is one of the isomers produced.

Name and outline a mechanism for the reaction producing pent-1-ene.

Name of mechanism _____

Mechanism

(4)

(f) A pair of stereoisomers is also formed in the reaction in **part (e)**.

Name the less polar stereoisomer formed.
Explain how this type of stereoisomerism arises.

Name _____

Explanation _____

_____

_____

(2)

(Total 16 marks)

Q14.

Concentrated sulfuric acid reacts with alkenes, alcohols and sodium halides.

(a) Name the mechanism for the reaction of concentrated sulfuric acid with an alkene.

_____

(1)

(b) Outline the mechanism for the reaction of concentrated sulfuric acid with propene to show the formation of the major product.

(4)

(c) Draw the structure of the minor product of the reaction between concentrated sulfuric acid and propene.

(1)

(d) Explain why the product shown in your answer to part (b) is the major product.

_____

_____

_____

_____

_____

_____

(2)

(e) Butan-2-ol reacts with concentrated sulfuric acid to form a mixture of three isomeric alkenes. Two of the alkenes are stereoisomers.

Draw the skeletal formula of each of the three isomeric alkenes formed by the reaction of butan-2-ol with concentrated sulfuric acid.

Give the full IUPAC name of each isomer.

Skeletal formula	Name

(3)

(f) A by-product of the reaction of butan-2-ol with concentrated sulfuric acid has the molecular formula C_4H_8O

Name this by-product, identify the role of the sulfuric acid in its formation and suggest the name of a method that could be used to separate the products of this reaction.

By-product _____

_____

Role of sulfuric acid _____

_____

Name of separation method

_____

(3)

(g) Concentrated sulfuric acid reacts with solid sodium chloride.

Give the observation you would make in this reaction.

State the role of the sulfuric acid.

Observation with sodium chloride _____

_____

Role of sulfuric acid _____

_____

(2)

(h) Concentrated sulfuric acid reacts with solid sodium iodide, to produce several products.

Observations made during this reaction include the formation of a black solid, a yellow solid and a gas with the smell of bad eggs.

Identify the product responsible for each observation.

Black solid _____

Yellow solid _____

Gas _____

(3)

(Total 19 marks)

Q15.

Which statement about ethanal is correct?

A It reacts with Tollens' reagent to form silver. ⬭

B It has a higher boiling point than ethanol. ⬭

C Its empirical and molecular formulas are different. ⬭

D It belongs to a homologous series with general formula $C_nH_{2n+1}O$ ⬭

(Total 1 mark)

Q16.

Alcohol **A** $(CH_3)_2CHCH(OH)CH_3$ undergoes reactions separately with acidified potassium dichromate(VI) and with concentrated sulfuric acid.

(a) Deduce the IUPAC name for alcohol **A**.

_____

(1)

(b) Draw the structure of the organic product, **B**, formed when **A** is oxidised in the reaction with acidified potassium dichromate(VI).

(1)

(c) Two isomeric alkenes, **C** and **D**, are formed when **A** is dehydrated in the reaction with concentrated sulfuric acid.

Name the mechanism for this dehydration reaction.

_____

(1)

(d) Draw the structure of each isomer.

Isomer **C** Isomer **D**

(2)

(e) Name the type of structural isomerism shown by **C** and **D**.

_____

(1)

(f) List alcohol **A**, product **B** and isomer **C** in order of increasing boiling point.

_____

(1)

(g) Draw the structure of the isomer of **A** that is **not** oxidised by acidified potassium dichromate(VI).

(1)

(h) Draw the structure of the isomer of **A** that **cannot** be dehydrated to form an alkene by reaction with concentrated sulfuric acid.

(1)
(Total 9 marks)

Q17.

Ethanol can be oxidised by acidified potassium dichromate(VI) to ethanoic acid in a two-step process.

ethanol ⟶ ethanal ⟶ ethanoic acid

(a) In order to ensure that the oxidation to ethanoic acid is complete, the reaction is carried out under reflux.

Describe what happens when a reaction mixture is refluxed and why it is necessary, in this case, for complete oxidation to ethanoic acid.

(3)

(b) Write a half-equation for the overall oxidation of ethanol into ethanoic acid.

(1)

(c) The boiling points of the organic compounds in a reaction mixture are shown in the following table.

Compound	ethanol	ethanal	ethanoic acid
Boiling point / °C	78	21	118

Use these data to describe how you would obtain a sample of ethanal from a mixture of these three compounds. Include in your answer a description of the apparatus you would use and how you would minimise the loss of ethanal. Your description of the apparatus can be either a description in words or a labelled sketch.

(5)

(d) Use your knowledge of structure and bonding to explain why it is possible to separate ethanal in this way.

(2)

(e) A student obtained a sample of a liquid using the apparatus in part **(c)**.

Describe how the student could use chemical tests to confirm that the liquid contained ethanal and did **not** contain ethanoic acid.

_____

_____

_____

_____

_____

_____

_____

_____

(5)

(Total 16 marks)

Q18.

A Grignard reagent is a compound in which magnesium is bonded to an alkyl group (R) and a halogen (X). It can be represented by the formula RMgX.

A Grignard reagent is formed by the reaction of magnesium metal with a haloalkane using dry ethoxyethane as a solvent. Ethoxyethane has a boiling point of 35 ºC, forms a dense vapour and is highly flammable.

(a) Give **one** reason why a hot water bath is used rather than direct heating with a Bunsen burner when preparing the Grignard reagent.

_____

(1)

(b) Grignard reagents react with water.

Suggest **one** reason why the ethoxyethane protects the Grignard reagent from reacting with water vapour in the air.

_____

(1)

(c) A Grignard reagent can be used to introduce an extra carbon atom into an organic molecule.
For example, propanone (CH_3COCH_3) reacts with CH_3MgBr in a two-stage process to form 2-methylpropan-2-ol, $(CH_3)_3COH$. The isomer 2-methylpropan-1-ol is not formed in this process.

Suggest a suitable reagent and the associated observations that could be used to distinguish between 2-methylpropan-2-ol and its isomer 2-methylpropan-1-ol.

Reagent _____

Observation with 2-methylpropan-2-ol _____

_____

Observation with 2-methylpropan-1-ol _____

_____

(3)

(d) At the end of the preparation of the alcohol, the bromine from the Grignard reagent remains as the bromide ion.
Suggest reagents and observations to confirm that this halide ion is Br^- and not I^-

_____

_____

_____

_____

_____

_____

_____

_____

_____

(4)

(Total 9 marks)

Mark Scheme

Q12.

C

[1]

Q13.

(a) Aldehyde/propanal has dipole-dipole forces (between molecules)

If any 'covalent bonds broken' CE=0 for clip.

Ignore Van der Waal forces

M1

Alcohol/propan-1-ol AND Carboxylic acid/ propanoic acid have hydrogen bonding (between molecules).

Ignore reference to energy

M2

The forces between the molecules in aldehyde are weaker (than those in alcohol and acid so it will evaporate first.)

M3 only awarded following correct M1 OR M2

Allow converse for M3

M3

(b) Keep the temperature of the reaction mixture below the boiling point of propan-1-ol/below 97 °C

Allow temperature in range 49-96 inclusive

Allow description of cooling the vessel

M1

Cool the distillate / collecting vessel

Ignore reference to oxidising agents

Penalise lid / sealed container

M2

(c) Add named carbonate/hydrogencarbonate OR magnesium to a sample of the distillate.

Incorrect chemical CE=0

Allow formula (mark on for incorrect formula)

Allow blue litmus or correct named indicator

M1

Effervescence/fizz/bubbles would confirm presence of acid or converse

Blue litmus turns red confirms acid present or converse

Allow gas/CO_2 produced which turns lime water cloudy OR gas/H_2 produced which burns with a squeaky pop

M2

(d) (Temperature difference = 15.1 °C)

If ΔT wrong – AE mark on otherwise can only award M2

If use 457 in M1, can only score M2

q = 150 × 4.18 × 15.1 or 9467.7 J or 9.4677kJ

M1

amount ethanol burned = 0.457/46.0 = 9.93×10^{-3} mol

If use 457 in M2 can score 2 for - 0.953 kJ mol-1

M2

Heat change per mole = (M1/1000)/M2 = 952.99 kJ mol-1

ΔH = – 953 kJ mol^{-1} must be 3sfs and must be negative

(allow range -953 to -954)

BEWARE if they miss conversion to kJ and also miss conversion to g, they get answer = - 953 which scores 1
+953 can score M1 and M2
Allow -950 or -960 for rounding to 2sf

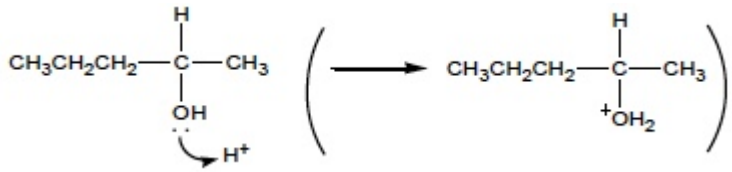
M3

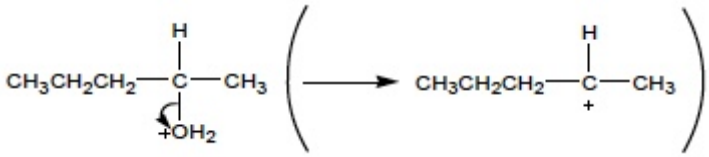
(e) Elimination

Penalise base elimination

M1

Mechanism : Either (E1)

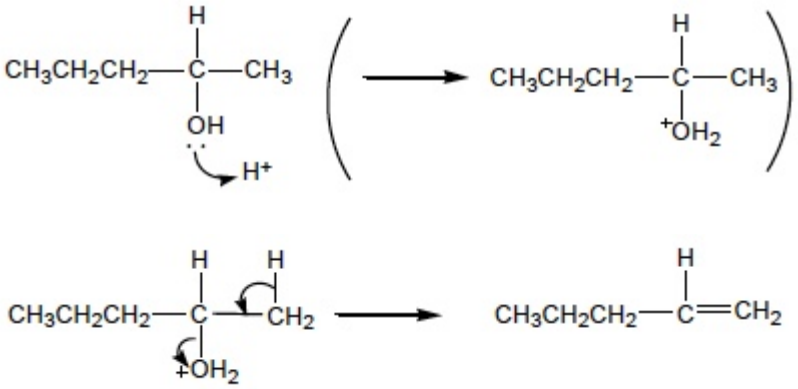




M2 for protonation of alcohol, i.e. lp plus arrow to H^+
or to H of H–O– in H_2SO_4 and from H-O bond to O
M3 for protonated alcohol plus arrow showing loss of water
M4 for arrow showing loss of H^+
From correct carbocation (E1)
wrong alcohol used / alkene formed loses M4

3

OR (E2)



M2 for protonation of alcohol, i.e. lp plus arrow to H^+ or to H of H–O– in H_2SO_4 and from H-O bond to O
M3 for protonated alcohol plus arrow showing loss of water
M4 for arrow showing simultaneous loss of H^+
wrong alcohol used / alkene formed loses M4

3

(f) *E*-pent-2-ene

Allow trans

M1

C=C bond cannot <u>rotate</u> **and**

Each carbon in the double bond has (2) different groups attached.

Allow (two) different groups on each/either side of the double bond.

M2

[16]

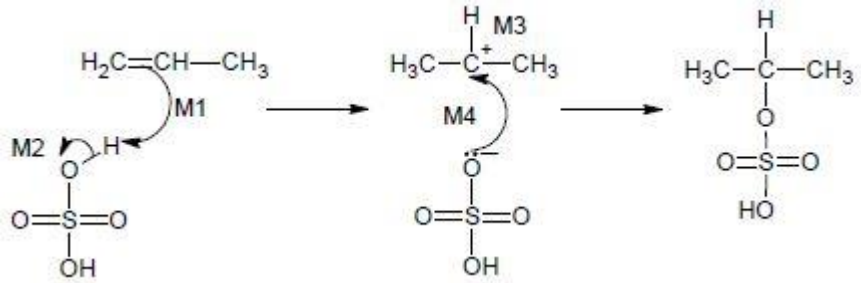
Q14.

(a) <u>electrophilic addition</u>

ALLOW phonetic e.g. electrophylic, electrophillic

1

(b)



M1: must show an arrow from = of C=C towards the H atom of the H–O bond or HO that is part of H–O–S–… on a compound with molecular formula H_2SO_4
M1 could have arrow to H^+ in which case **M2** would be for an independent H–O bond break on a compoundwith formula H_2SO_4

ALLOW CH_3–C^+ etc for carbocation

No need for hydrogensulfate to be displayed

*If H_2O used as electrophile – max **M3** ONLY*

M2: must use an arrow to show the breaking of the H–O bond

***M2** ignore partial charges unless wrong*

M3: is for the correct carbocation structure

*NOT **M3** if primary carbocation shown.*

M4: must show an arrow from a lone pair of electrons on the correct oxygen of the negatively charged ion towards the positively charged carbon atom

***M4** NOT HSO_4*

credit as shown (or $^{-}$:OSO_2OH)

or as :OSO_3H – in which case negative charge can be shown anywhere

*ecf from H_2SO_3 in **M1***

NB: The arrows are double-headed

***IGNORE** subsequent use of water to hydrolyse hydrogensulfate*

4

(c) minor product = $CH_3CH_2CH_2OSO_3H$

ecf from 1° in (b) for $CH_3CH(OSO_3H)CH_3$

ecf from alcohol as product in (b)

ecf from side chain such as –$OHSO_3$ or –HSO_4 in (b)

1

(d) (major) product formed via more stable carbocation OR secondary carbocation more stable (than primary)

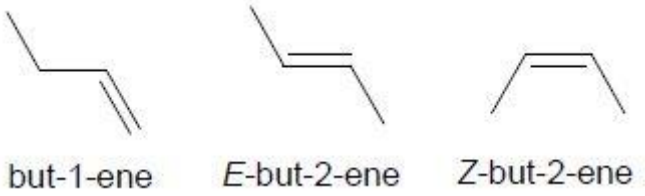
1

Due to electron-releasing character / (positive) inductive effect of two alkyl / methyl groups (as opposed to one)

1

ALLOW 'more' alkyl groups in place of 'two' alkyl groups

(e)



*matching name **and** formula for each mark*

One 'salvage' mark available for 3 correct structures or 3 correct names if no other mark awarded

*use of trans **and** cis can score 1/2 for the two but-2-ene structures*

3

(f) butanone

ALLOW butan-2-one

1

oxidising agent

ALLOW electron acceptor but NOT electron pair acceptor

1

(fractional) distillation

ALLOW gas chromatography

1

(g) white / misty / steamy fumes

NOT gas evolved / effervescence

1

acid/proton donor

1

(h) iodine / I_2

IGNORE state symbols

1

sulfur / S / S_8

*If name **and** formula given they must both be right*

1

hydrogen sulfide / H_2S

1

[19]

Q15.

A

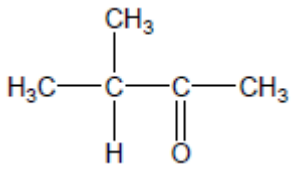
[1]

Q16.

(a) 3-methylbutan-2-ol

1

(b)



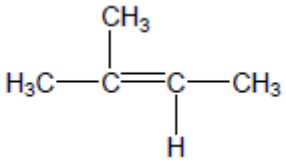
Allow $(CH_3)_2CHCOCH_3$

1

(c) Elimination

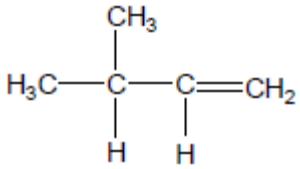
1

(d)



Allow $(CH_3)_2C=CHCH_3$

1



Allow $(CH_3)_2CHCH=CH_2$

1

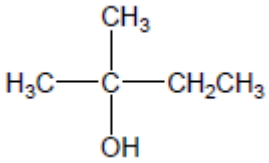
(e) Position

1

(f) C B A

1

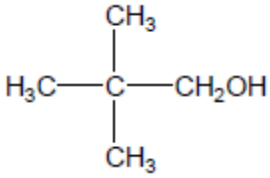
(g)



Allow $(CH_3)_2C(OH)CH_2CH_3$

1

(h)



Allow $(CH_3)_3CCH_2OH$

1

[9]

Q17.

(a) A mixture of liquids is heated to boiling point for a prolonged time

1

Vapour is formed which escapes from the liquid mixture, is changed back into liquid and returned to the liquid mixture

1

Any ethanal and ethanol that initially evaporates can then be oxidised

1

(b) $CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + 4H^+ + 4e^-$

1

(c) Mixture heated in a suitable flask / container

A labelled sketch illustrating these points scores the marks

1

With still head containing a thermometer

1

Water cooled condenser connected to the still head and suitable cooled collecting

vessel

1

Collect sample at the boiling point of ethanal

1

Cooled collection vessel necessary to reduce evaporation of ethanal

1

(d) Hydrogen bonding in ethanol and ethanoic acid or no hydrogen bonding in ethanal

1

Intermolecular forces / dipole-dipole are weaker than hydrogen bonding

1

(e) Reagent to confirm the presence of ethanal:

Add Tollens' reagent / ammoniacal silver nitrate / aqueous silver nitrate followed by 1 drop of aqueous sodium hydroxide, then enough aqueous ammonia to dissolve the precipitate formed

OR

Add Fehling's solution

1

Warm

M2 and M3 can only be awarded if M1 is given correctly

1

Result with Tollen's reagent:

Silver mirror / black precipitate

OR

Result with Fehling's solution:

Red precipitate / orange-red precipitate

1

Reagent to confirm the absence of ethanoic acid

Add sodium hydrogencarbonate or sodium carbonate

1

Result; no effervescence observed; hence no acid present

1

M5 can only be awarded if M4 is given correctly

OR

Reagent; add ethanol and concentrated sulfuric acid and warm

Result; no sweet smell / no oily drops on the surface of the liquid,

hence no acid present

[16]