Q1.

The skeletal formulas of two compounds are shown.

Which method would distinguish between samples of these compounds?

A comparing fingerprint regions of their infrared spectra ⬭

B obtaining molecular masses from their high resolution mass spectra ⬭

C warming with acidified potassium dichromate(VI) solution ⬭

D warming with Tollens' reagent ⬭

(Total 1 mark)

Q2.

An acidified solution of butanone reacts with iodine as shown.

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

(a) Draw the displayed formula for $CH_3CH_2COCH_2I$

Give the name of $CH_3CH_2COCH_2I$

Displayed formula

Name _____

(2)

(b) The rate equation for the reaction is

$$rate = k[CH_3CH_2COCH_3][H^+]$$

Table 1 shows the initial concentrations used in an experiment.

Table 1

	$CH_3CH_2COCH_3$	**I_2**	**H^+**
Initial concentration / mol dm^{-3}	4.35	0.00500	0.825

The initial rate of reaction in this experiment is 1.45×10^{-4} mol dm^{-3} s^{-1}

Calculate the value of the rate constant, *k*, for the reaction and give its units.

k _____

Units _____

(3)

(c) Calculate the initial rate of reaction when all of the initial concentrations are halved.

Initial rate of reaction _____ mol dm^{-3} s^{-1}

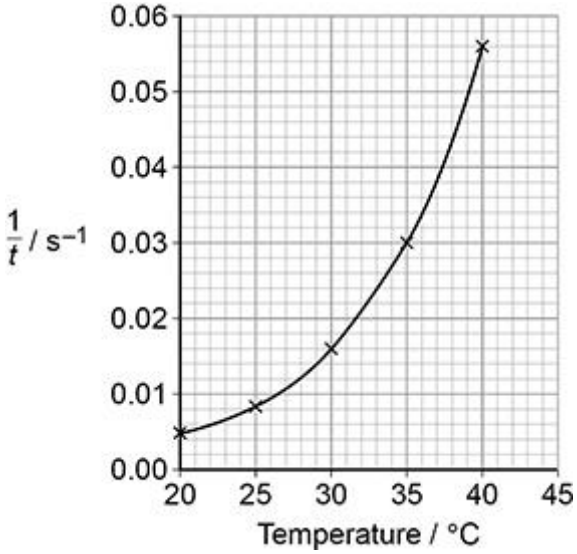
(1)

(d) An experiment was done to measure the time, *t*, taken for a solution of iodine to react completely when added to an excess of an acidified solution of butanone.

Suggest an observation used to judge when all the iodine had reacted.

The experiment was repeated at different temperatures.

The graph below shows how $\frac{1}{t}$ varied with temperature for these experiments.



(1)

(e) Describe and explain the shape of the graph above.

(3)

(f) Deduce the time taken for the reaction at 35 °C

Time _____ s

(1)

(g) For a different reaction, **Table 2** shows the value of the rate constant at different temperatures.

Table 2

Experiment	Temperature / K	Rate constant / s^{-1}
1	$T_1 = 303$	$k_1 = 1.55 \times 10^{-5}$
2	$T_2 = 333$	$k_2 = 1.70 \times 10^{-4}$

This equation can be used to calculate the activation energy, E_a

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Calculate the value, in kJ mol^{-1}, of the activation energy, E_a

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

E_a _____ kJ mol^{-1}

(5)

(h) Name and outline the mechanism for the reaction of butanone with KCN followed by dilute acid.

Name of mechanism _____

Outline of mechanism

(5)

(Total 21 marks)

Q3.

This question is about ketones.

(a) Solution **X** reacts with liquid ketones to form a crystalline solid.

This reaction can be used to identify a ketone if the crystalline solid is separated, purified by recrystallisation, and the melting point determined.

Describe how the crystalline solid is separated and purified.

(5)

(b) Propanone (CH_3COCH_3) reacts with the weak acid HCN to form a hydroxynitrile.

This hydroxynitrile is usually made by reaction of propanone with KCN followed by dilute acid, instead of with HCN

State the hazard associated with the use of KCN

Suggest a reason, other than safety, why KCN is used instead of HCN.

Hazard _____

Why KCN is used _____

(2)

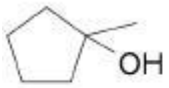
(c) Outline the mechanism for the reaction of propanone with KCN followed by dilute acid.

(4)
(Total 11 marks)

Q4.

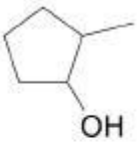
This question is about the structural isomers shown.

P

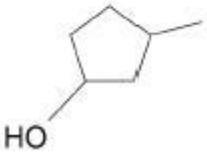


Q

R

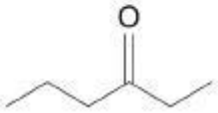


S



T

U



(a) Identify the isomer(s) that would react when warmed with acidified potassium dichromate(VI).

State the expected observation when acidified potassium dichromate(VI) reacts.

Isomer(s) _____

Expected observation _____

_____

(2)

(b) Identify the isomer(s) that would react with Tollens' reagent.

State the expected observation when Tollens' reagent reacts.

Isomer(s) _____

Expected observation _____

_____

(2)

(c) Separate samples of each isomer are warmed with ethanoic acid and a few drops of concentrated sulfuric acid. In each case the mixture is then poured into a solution of sodium hydrogencarbonate.

Identify the isomer(s) that would react with ethanoic acid.

Suggest a simple way to detect if the ethanoic acid reacts with each isomer.

Give a reason why the mixture is poured into sodium hydrogencarbonate solution.

Isomer(s) _____

Suggestion _____

_____

Reason _____

_____

(3)

(d) State the type of structural isomerism shown by isomers **P**, **Q**, **R** and **S**.

_____

(1)

(e) Describe fully how infrared spectra can be used to distinguish between isomers **R**, **S** and **T**.
Use data from **Table A** in the Data Booklet in your answer.

_____

_____

_____

_____

_____

_____

_____

(4)

(f) State why mass spectrometry using electrospray ionisation is **not** a suitable method to distinguish between the isomers.

_____

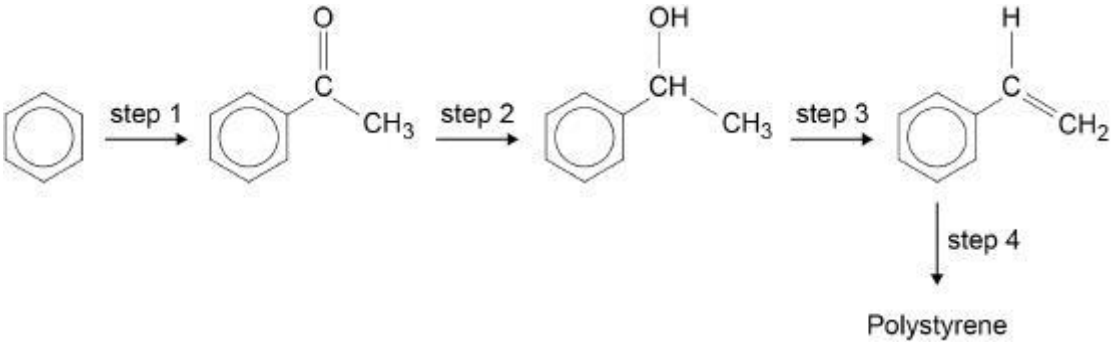
_____

(1)

(Total 13 marks)

Q5.

Polystyrene can be made from benzene in the series of steps shown.



(a) State the type of reaction in step **1**.

Identify the reagent(s) and conditions needed for step **1**.

Type of reaction _____

Reagent(s) _____

Conditions _____

(3)

(b) State the name of the mechanism for the reaction in step **2**.

Identify the inorganic reagent needed for step **2**.

Name the organic product of step **2**.

Name of mechanism _____

Inorganic reagent _____

Name of organic product _____

(3)

(c) The organic product of step **2** is reacted with concentrated sulfuric acid in step **3**.

Outline the mechanism for step **3**.

(3)

(d) Draw the repeating unit of polystyrene.

(1)

(Total 10 marks)

Q6.

Aqueous $NaBH_4$ reduces aldehydes but does not reduce alkenes.

(a) Show the first step of the mechanism of the reaction between $NaBH_4$ and 2-methylbutanal.
You should include two curly arrows.

Explain why $NaBH_4$ reduces 2-methylbutanal but has no reaction with 2-methylbut-1-ene.

First step of mechanism

Explanation _____

_____

_____

_____

_____

_____

_____

(5)

(b) A student attempted to reduce a sample of 2-methylbutanal but added insufficient $NaBH_4$
The student confirmed that the reduction was incomplete by using a chemical test.

Give the reagent and observation for the chemical test.

Reagent _____

_____

Observation _____

_____

(2)

(Total 7 marks)

Q7.

Ethanal reacts with potassium cyanide, followed by dilute acid, to form 2-hydroxypropanenitrile.

(a) Name the mechanism for the reaction between potassium cyanide and ethanal.

_____

(1)

(b) The 2-hydroxypropanenitrile formed by the reaction in part **(a)** is a mixture of equal amounts of two isomers.

State the name of this type of mixture.

Explain how the structure of ethanal leads to the formation of two isomers.

Draw 3D representations of the two isomers to show the relationship between them.

Name _____

Explanation _____

_____

_____

_____

_____

_____

3D representations

(5)

(c) 2-Hydroxypropanenitrile can be used in the synthesis of the monomer, acrylonitrile, CH_2=CHCN

Suggest a suitable reagent and conditions for the conversion of 2-hydroxypropanenitrile into acrylonitrile.

Reagent _____

Conditions _____

(2)

(d) Draw a section of the polymer polyacrylonitrile, showing three repeating units.

(1)

(Total 9 marks)

Mark schemes

Q1.

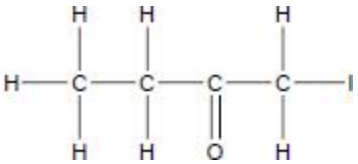
A

comparing fingerprint regions of their infrared spectra

[1]

Q2.

(a)



Apply list principle for more than one structure given

M1

1-iodobutan-2-one

Allow 1-iodo-2-butanone

M2

(b) $\frac{\text{Rate}}{[CH_3CH_2COCH_3][H^+]} = k$

Rearranged expression Or with numbers

M1

k = 4.(04) × 10^{-5} or 0.00004(04)

If upside down = 24752 mol dm^{-3} s

If multiply = 5.20 × 10^{-4} mol^3 dm^{-9} s^-

M2

mol^{-1} dm^3 s^{-1}

M3

(c) 3.6(25) × 10^{-5} (mol dm^{-3} s^{-1})

Allow 3.59 × 10^{-5} to 3.63 × 10^{-5}

1

(d) Brown colour removed

Goes colourless

Allow (orange) brown to colourless

Allow purple to colourless

1

(e) As T increases rate (1/t) increases OR time for completion decreases

M1

Exponentially
OR
By a greater/ increasing factor

Or rate increases more and more as temp increases ie description of exponential increase

M2

Many more particles have $E \geq E_a$

NOT just higher collision frequency

NOT just more successful collisions

M3

(f) Time = $\frac{1}{0.03}$ = 33 s

1

(g) $\ln(1.55 \times 10^{-5}/1.70 \times 10^{-4}) = \frac{E_a}{R}\left(\frac{1}{333} - \frac{1}{303}\right)$

Insertion of correct values

M1

$-2.39 = \frac{E_a}{R}(-2.97 \times 10^{-4})$

Evaluate LHS and fraction on RHS

M2

$\frac{2.39 \times 8.31}{2.97 \times 10^{-4}} = E_a$

Re-arrange for E_a

M3

66937

Evaluate

M4

66.9 kJ mol^{-1}

convert to kJ mol^{-1}

M5

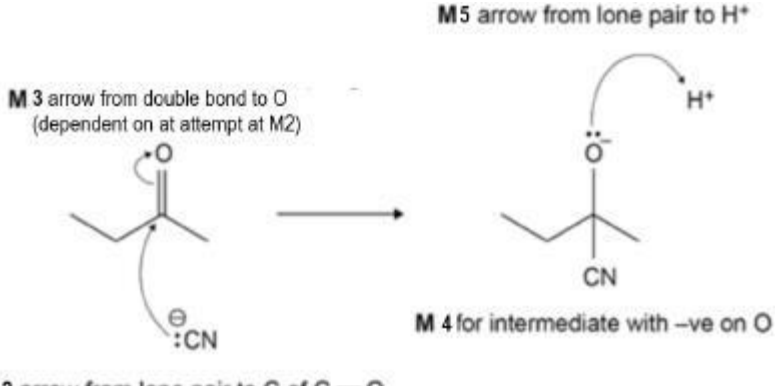
If only k_1 and k_2 reversed this gives a negative answer for E_a Lose M1 and M5

If AE in M2 allow ECF

Allow ECF from M4 to M5 for a correct unit conversion

Allow range 66.3 − 67.1

(h) Nucleophilic Addition



M1M2M3M4M5

ALLOW negative charge anywhere on cyanide
But attacking lone pair must be on C
Do not award M3 without attempt of M2
Allow M2 for attack to a positive carbon following breaking of C=O
Penalise covalent KCN in M2
M3 ignore partial charges unless wrong
Penalise M3 for incorrect connection between CN and C
NB Allow fully displayed or other structural formulae

[21]

Q3.

(a) filter / decant

1

dissolve in minimum vol

allow *small volume*
allow *to make saturated solution*
not *warm*
Ignore *hot filtration*

1

of hot solvent

1

cool / leave (to crystallise) **AND** filter (under reduced pressure)

1

Wash with cold solvent/water, and dry (with method)

1

(b) **M1** toxic / poisonous

allow *can produce toxic fumes/gas / corrosive*

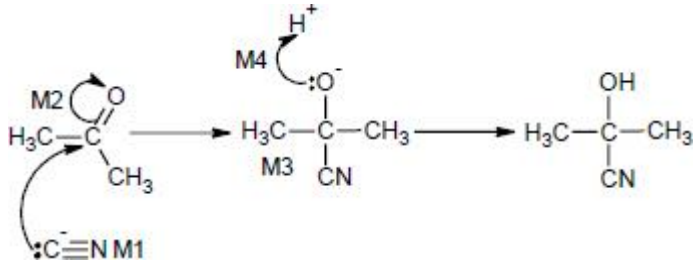
1

M2 HCN weak / [CN^-] too low **ORA**

allow *KCN dissociates to provide CN^-/nucleophile*
allow *KCN dissociates better/more than HCN*

1

(c)



M1 cyanide ion with lone pair on C and negative charge and curly arrow from lone pair to C of C=O

not *if K−CN bond shown breaking*

1

M2 Curly arrow from = to O

not *if dipole incorrect*

1

M3 intermediate anion

new bond must be to C of CN

1

M4 curly arrow from lone pair on O to H^+

allow *curly arrow to H of HCN*

1

[11]

Q4.

(a) **M1** Q, R, S, T

M1 Allow the mark for candidates who correctly name or draw the isomers.

1

M2 (Orange solution) turns green

Independent

1

(b) **M1** T

As above

1

M2 Silver mirror

Allow grey/black ppt

1

(c) **M1** P, Q, R, S

As above

1

M2 Sweet smelling (liquid)

1

M3 To react with (remove excess) acid / neutralise

Allow easier to identify the smell

1

(d) Position

Allow positional

1

(e) **M1** R & S have an <u>O-H alcohols</u> peak at <u>3230-3550</u> cm^{-1}

Allow value within the range

1

M2 T has <u>C=O</u> peak at <u>1680-1750</u> cm^{-1}

1

M3 R & S (unique) fingerprint region or below 1500 cm^{-1}

1

M4 Compare to a database / known spectra (and look for an exact match)

1

(f) All have the same M_r

Allow

same (molecular) ion M/Z peak

same molecular formula

1

[13]

Q5.

(a) **M1** Acylation

Allow electrophilic substitution

Allow ethanoic anhydride for M2

1

M2 CH_3COCl OR Ethanoyl chloride

M3 dependent on M2

1

M3 $AlCl_3$ OR Aluminium chloride (mark could be awarded in space for M2)

Allow Dry/anhydrous for M3

Apply list principle to extra incorrect conditions

1

(b) **M1** Nucleophilic addition

1

M2 $NaBH_4$

Allow $LiAlH_4$ for M2

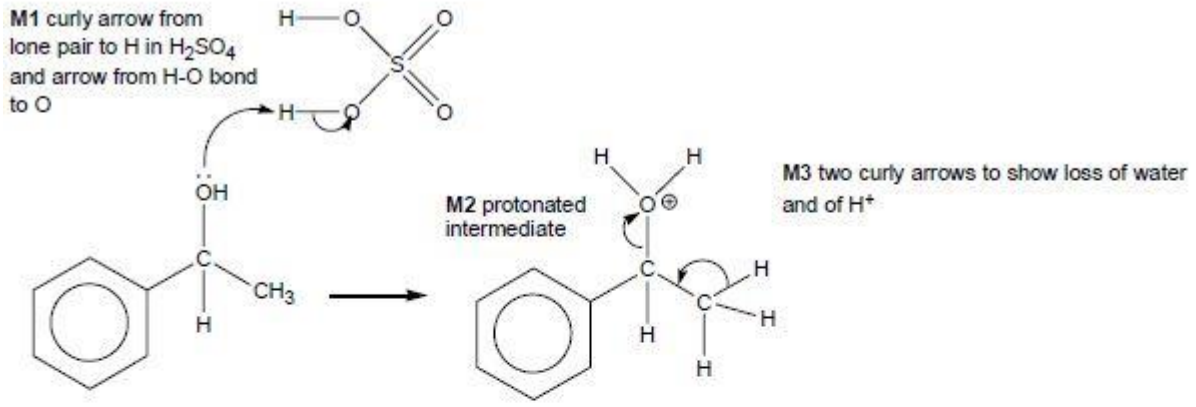
1

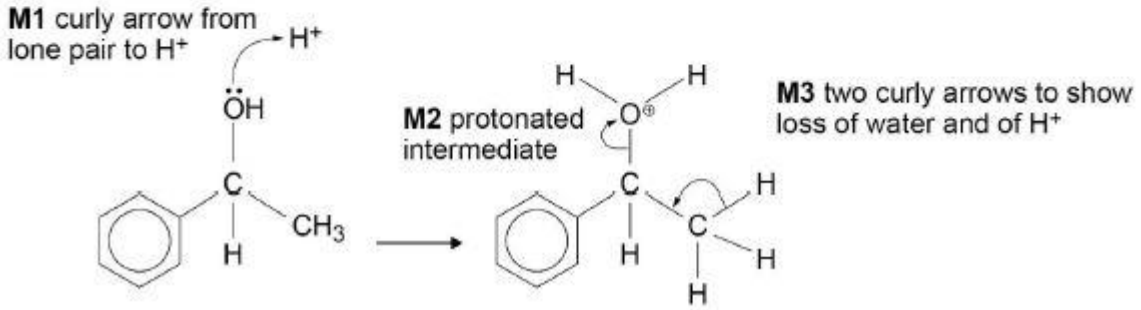
M3 1-phenyl ethan(-1-)ol

If H_2/Ni stated allow M2 and M3 but to score a matching M1 it would have to be Catalytic addition

1

(c)

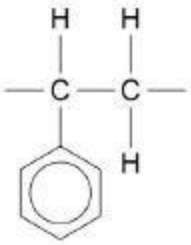




*Penalise **M1** for mistakes on structure of H_2SO_4*
*Allow H^+ attacked in **M1***
*Allow **M3** as two steps*
Allow displayed formulae

3

(d)



Must show trailing bonds
Ignore brackets and any use of n
Allow C_6H_5 for phenyl group

1

[10]

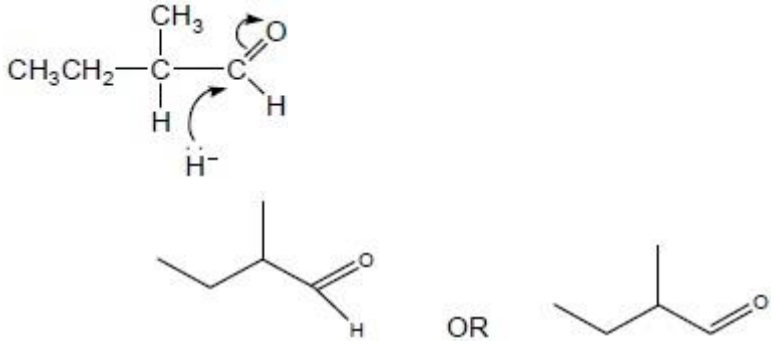
Q6.

(a) **M1** for structure of 2-methylbutanal

Allow C_2H_5 for CH_3CH_2

1

M2 for **2** curly arrows and lp on hydride, i.e.



1

Explanation:

*Penalise **M2** for wrong partial charges on C=O*

Ignore product

M3 H^- ion / nucleophile is attracted to δ+ C

1

M4 electron rich C=C

1

M5 H^- ion / nucleophile is repelled by C=C
OR
C=C only attacked by/reacts with electrophiles

1

(b) Tollens' (reagent) OR ammoniacal silver nitrate OR description of making Tollens'

1

Silver mirror/ppt OR black solid / precipitate / deposit

1

NOT dichromate

For Tollens' reagent:

*for **M1** ignore either $AgNO_3$ or $[Ag(NH_3)_2^+]$ or "the silver mirror test" on their own, or "Tolling's reagent", but mark on*

OR Fehling's/ Benedict's (solutions)

red solid / precipitate (allow orange or brown)

For Fehling's/Benedict's solution:

*for **M1** Ignore $Cu^{2+}(aq)$ or $CuSO_4$ or "Fellings" on their own, but mark on*

[7]

Q7.

(a) nucleophilic addition

both words needed

NOT any additional names

1

(b) **M1** racemic (mixture) / racemate

1

M2 planar (around) carbonyl / C=O

M2 *NOT molecule is planar*

Allow flat for planar

1

M3 (equal chance of) attack from each side (by CN^-)

1

M4 a correct structure of 2-hydroxypropanenitrile

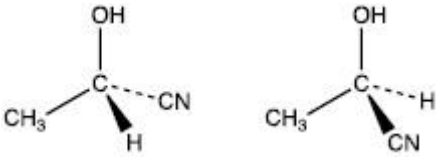
M4 *any correct 2D or 3D structure*

1

M5 correct 3D representations of both isomers, e.g.

M5 *must show at least one wedge bond and one dash bond in each structure and any bonds in the plane cannot be at 180º to each other*

second structure could be drawn as mirror image of first ***or*** *with same orientation with two groups swapped round, e.g.*



Allow ECF for second structure from incorrect first structure, providing molecule is chiral

1

(c) **M1** conc H_2SO_4 or conc H_3PO_4

M1 *Allow conc to come from conditions line*

1

M2 heat / 170°C

M2 *depends on attempt at correct reagent in* ***M1***

Allow high temperature / hot / 100-300°C / 373 – 573 K / reflux

Ignore references to pressure

Ignore warm

NOT ethanolic / alcoholic

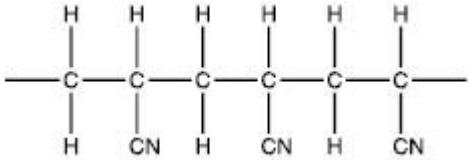
1

Alternative answer

M1 Al_2O_3

M2 *pass vapour over hot* Al_2O_3

(d)



MUST show trailing bonds
Ignore any brackets or n
NOT C–N or C=N if CN group displayed
Allow structures with CN on either C in each of the three units
Allow –CH_2–CH(CN)–CH_2–CH(CN)–CH_2–CH(CN)–

1

[9]