Q1.

Which compound is an amide?

A $CH_3CH_2CH_2CN$ ⬭

B $CH_3CONHCH_2CH_3$ ⬭

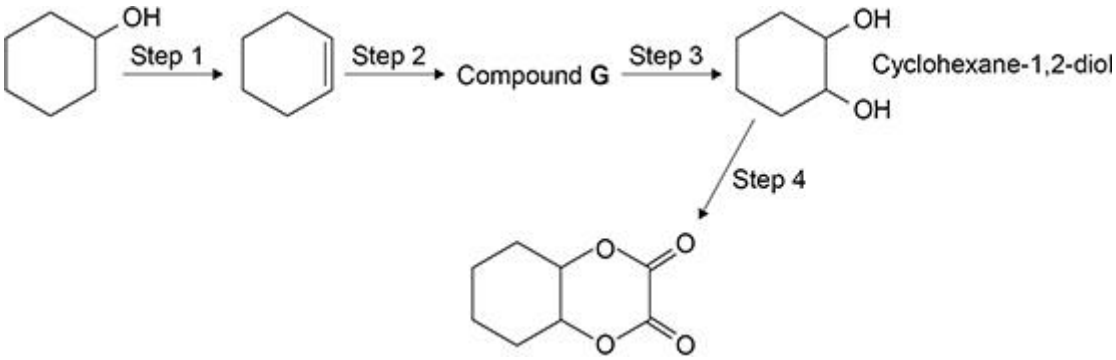
C $CH_3COOCH_2CH_3$ ⬭

D $CH_3NHCH_2CH_2CH_3$ ⬭

(Total 1 mark)

Q2.

This question is about making a diester from cyclohexanol.



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

Give the name of the reagent needed for step **1**.

Type of reaction _____

Reagent _____

(2)

(b) State the reagents needed and give equations for step **2** and step **3**.

Show the structure of Compound **G** in your equations.

Step 2 reagent _____

Step 2 equation

_____

Step 3 reagent _____

Step 3 equation

_____

(4)

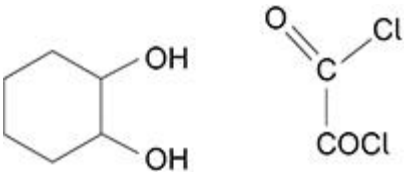
(c) Cyclohexane-1,2-diol reacts with ethanedioyl dichloride.

Give the name of the mechanism for this reaction.

Complete the mechanism to show the formation of **one** ester link in the first step of this reaction.

Mechanism name _____

Mechanism



(5)

(d) Suggest why chemists usually aim to design production methods

- with fewer steps
- with a high percentage atom economy.

Fewer steps _____

_____

_____

High percentage atom economy _____

_____

_____

(2)

(Total 13 marks)

Q3.

Which compound forms a white precipitate when added to aqueous silver nitrate?

A bromoethane ⬭

B ethanal ⬭

C ethanoic anhydride ⬭

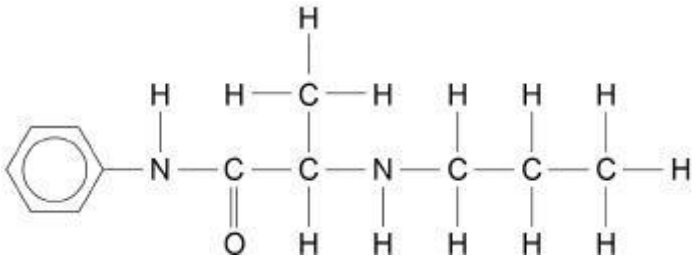
D ethanoyl chloride ⬭

(Total 1 mark)

Q4.

Prilocaine is used as an anaesthetic in dentistry.
Figure 1 shows the structure of prilocaine.

Figure 1



(a) Draw a circle around any chiral centre(s) in **Figure 1**.

(1)

(b) Identify the functional group(s) in the prilocaine molecule.

Tick (✓) the box(es) corresponding to the functional group(s).

Amide	Amine	Ester	Ketone

(1)

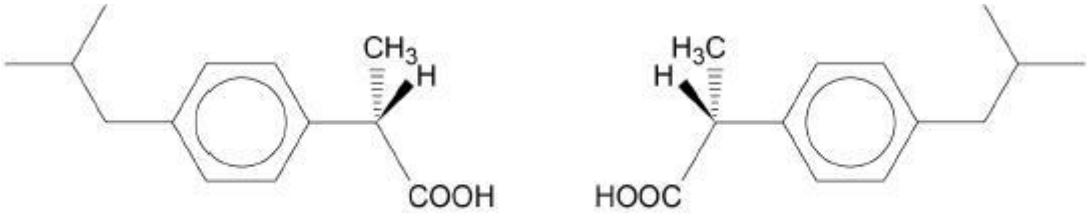
(c) Prilocaine is completely hydrolysed in the human body to give a mixture of products.

Draw the structures of the two organic products formed in the complete hydrolysis of prilocaine in acidic conditions.

(3)

(d) **Figure 2** shows optical isomers **F** and **G**.

Figure 2



Isomer **F** Isomer **G**

Isomer **F** is the active compound in the medicine ibuprofen.

In the manufacture of ibuprofen both isomers **F** and **G** are formed. An enzyme is then used to bind to isomer **G** and catalyse its hydrolysis.

After the products of hydrolysis of **G** are removed, a pure sample of isomer **F** is collected.

Explain how a structural feature of this enzyme enables it to catalyse the hydrolysis of isomer **G** but not the hydrolysis of isomer **F**.

_____

_____

_____

_____

(2)

(Total 7 marks)

Q5.

Aspirin can be produced by reacting salicylic acid with ethanoic anhydride.
An incomplete method to determine the yield of aspirin is shown.

1. Add about 6 g of salicylic acid to a weighing boat.
2. Place the weighing boat on a 2 decimal place balance and record the mass.
3. Tip the salicylic acid into a 100 cm^3 conical flask.
4. _____
5. Add 10 cm^3 of ethanoic anhydride to the conical flask and swirl.
6. Add 5 drops of concentrated phosphoric acid.
7. Warm the flask for 20 minutes.
8. Add ice-cold water to the reaction mixture and place the flask in an ice bath.
9. Filter off the crude aspirin from the mixture and leave it to dry.
10. Weigh the crude aspirin and calculate the yield.

(a) Describe the instruction that is missing from step **4** of the method.

Justify why this step is necessary.

Instruction _____

Justification _____

_____

_____

(2)

(b) Suggest a suitable piece of apparatus to measure out the ethanoic anhydride in step **5**.

_____

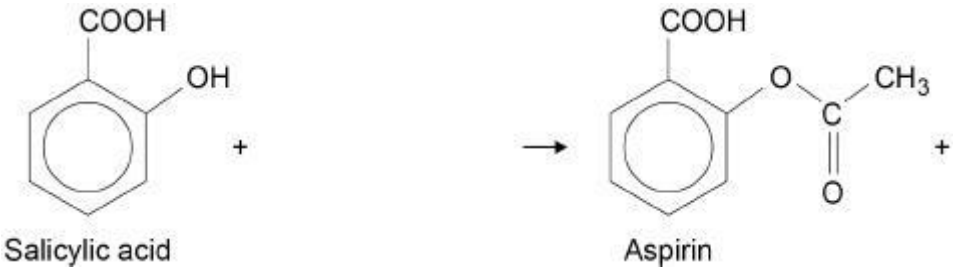
(1)

(c) Identify a hazard of using concentrated phosphoric acid in step **6**.

_____

(1)

(d) Complete the equation for the reaction of salicylic acid with ethanoic anhydride to produce aspirin.



(1)

(e) A 6.01 g sample of salicylic acid (M_r = 138.0) is reacted with 10.5 cm^3 of ethanoic anhydride (M_r = 102.0).
In the reaction the yield of aspirin is 84.1%

The density of ethanoic anhydride is 1.08 g cm^{-3}

Show by calculation which reagent is in excess.

Calculate the mass, in g, of aspirin (M_r = 180.0) produced.

Reagent in excess _____

Mass of aspirin _____ g

(5)

(f) Suggest **two** ways in which the melting point of the crude aspirin collected in step **9** would differ from the melting point of pure aspirin.

Difference 1 _____

_____

Difference 2 _____

_____

(2)

(g) The crude aspirin can be purified by recrystallisation using hot ethanol (boiling point = 78 °C) as the solvent.

Describe **two** important precautions when heating the mixture of ethanol and crude aspirin.

Precaution 1 _____

_____

Precaution 2 _____

_____

(2)

(h) The pure aspirin is filtered under reduced pressure.
A small amount of cold ethanol is then poured through the Buchner funnel.

Explain the purpose of adding a small amount of cold ethanol.

_____

_____

_____

(1)

(i) A sample of the crude aspirin is kept to compare with the purified aspirin.

Describe **one** difference in appearance you would expect to see between these two solid samples.

_____

_____

_____

(1)

(Total 16 marks)

Q6.

A and **B** react together to form an equilibrium mixture.

$$A(aq) + 2\ B(aq) \rightleftharpoons C(aq)$$

An aqueous solution containing 0.25 mol of **A** is added to an aqueous solution containing 0.25 mol of **B**.

When equilibrium is reached, the mixture contains 0.015 mol of **C**.

(a) Calculate the amount of **A** and the amount of **B**, in moles, in the equilibrium mixture.

Amount of **A** _____ mol

Amount of **B** _____ mol

(2)

(b) At a different temperature, another equilibrium mixture contains 0.30 mol of **A**, 0.25 mol of **B** and 0.020 mol of **C** in 350 cm^3 of solution.

Calculate the value of the equilibrium constant K_c

Deduce the units of K_c

K_c _____

Units _____

(4)

When an excess of water is added to chloroethanal, an equilibrium mixture is formed.

$$ClCH_2CHO(aq) + H_2O(l) \rightleftharpoons ClCH_2CH(OH)_2(aq)$$

An expression for an equilibrium constant (K) for the reaction under these conditions is

$$K = \frac{[ClCH_2CH(OH)_2]}{[ClCH_2CHO]}$$

(c) Suggest why an expression for K can be written without the concentration of water.

_____

_____

_____

(1)

(d) Distilled water is added to 4.71 g of chloroethanal (M_r = 78.5) to make 50.0 cm^3 of solution. The mixture is allowed to reach equilibrium.

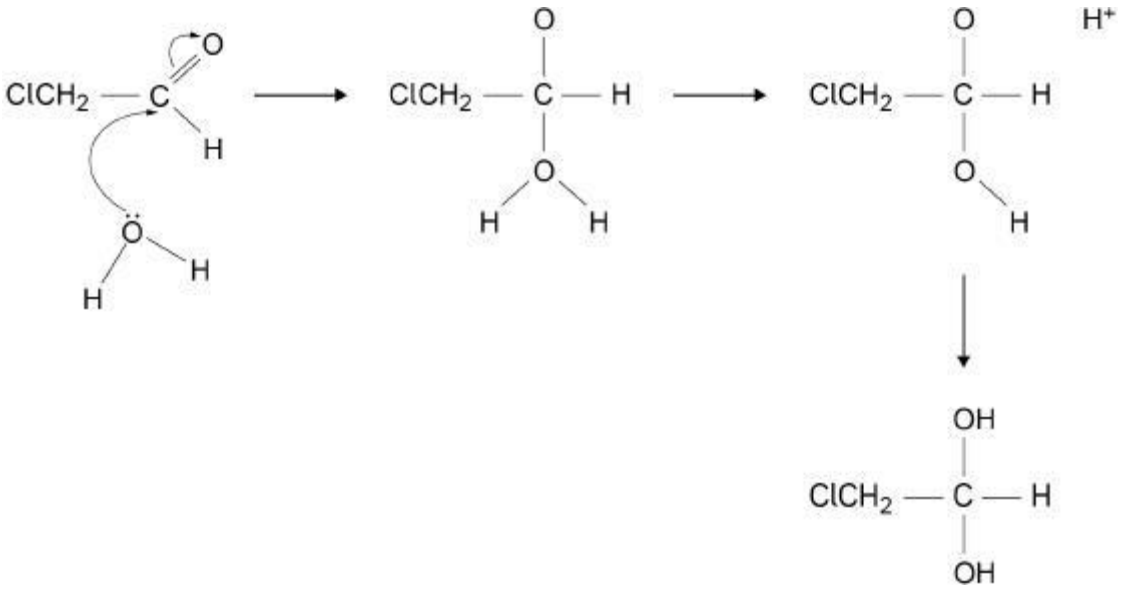
The value of the equilibrium constant (K) is 37.0

Calculate the equilibrium concentration, in mol dm^{-3}, of $ClCH_2CH(OH)_2$

Concentration _____ mol dm^{-3}

(5)

(e) The figure below shows an incomplete nucleophilic addition mechanism for the reaction of water with chloroethanal.



Complete the mechanism in the figure by adding **two** curly arrows, all relevant charges and any lone pairs of electrons involved.

(3)

(f) When an excess of water is added to ethanal a similar nucleophilic addition reaction occurs.

$CH_3CHO(aq) + H_2O(l) \rightleftharpoons CH_3CH(OH)_2(aq)$

Suggest why this reaction is slower than the reaction in part (e).

(3)

(Total 18 marks)

Q7.

Which reaction involves addition-elimination?

A $(CH_3)_2CHBr + KOH \rightarrow CH_3CH{=}CH_2 + KBr + H_2O$ ⬭

B $CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$ ⬭

C $CH_3CH{=}CH_2 + Cl_2 \rightarrow CH_3CHClCH_2Cl$ ⬭

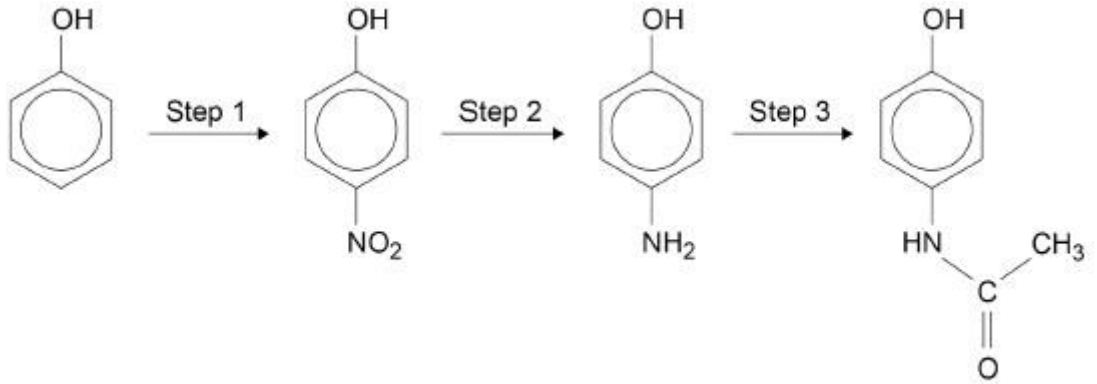
D $CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$ ⬭

(Total 1 mark)

Q8.

Paracetamol is a medicine commonly used to relieve mild pain.

Traditionally, paracetamol has been made industrially in a three-step synthesis from phenol.



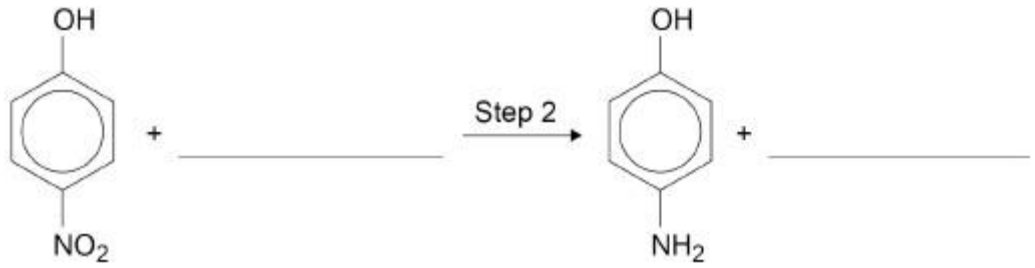
phenol 4-nitrophenol 4-aminophenol paracetamol

(a) Name the mechanism of the reaction in Step **1**.

_____

(1)

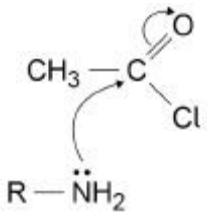
(b) Complete the equation for the reaction in Step **2**.



(1)

(c) In theory, either ethanoyl chloride or ethanoic anhydride could be used in Step **3**.

Complete the mechanism for the reaction of 4-aminophenol with ethanoyl chloride. RNH_2 is used to represent 4-aminophenol in this mechanism.



(2)

(d) In practice, ethanoic anhydride is used in the industrial synthesis rather than ethanoyl chloride.

Give **one** reason why ethanoyl chloride is **not** used in the industrial synthesis.

_____

_____

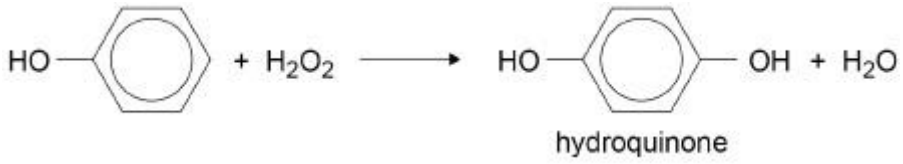
(1)

(e) In Step **3** other aromatic products are formed as well as paracetamol.

Draw the structure of **one** of these other aromatic products.

(1)

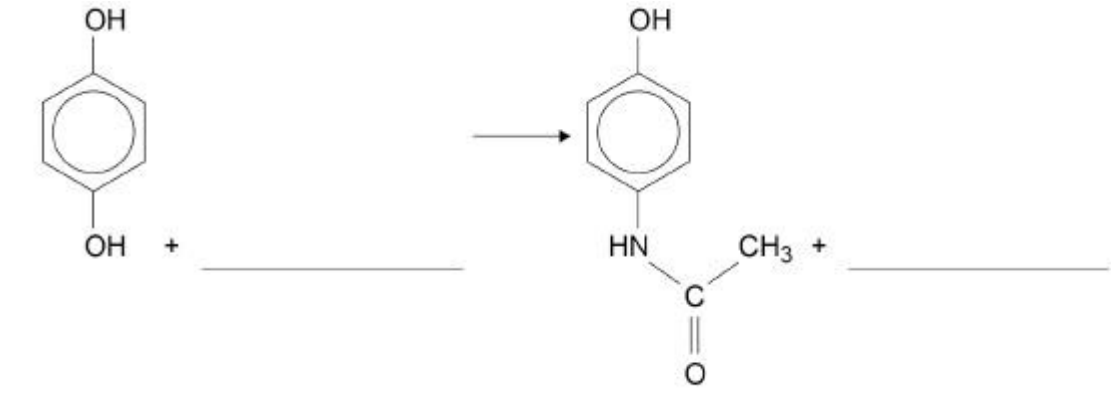
(f) Chemists have recently developed a two-step process to produce paracetamol from phenol.
In the first step, phenol is oxidised to hydroquinone.



hydroquinone

In the second step, hydroquinone reacts with ammonium ethanoate to form paracetamol.

Complete the equation for this second step.



hydroquinone paracetamol

(1)

(g) Calculate the mass, in kg, of hydroquinone (M_r = 110.0) needed to produce 250 kg of paracetamol.

Mass _____ kg

(3)

(Total 10 marks)

Mark schemes

Q1.

B

$CH_3CONHCH_2CH_3$

[1]

Q2.

(a) Dehydration

Allow (acid catalysed) Elimination

M1

Conc H_2SO_4

Allow Conc H_3PO_4

M2

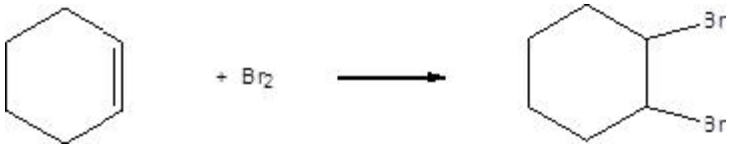
(b) Br_2

Allow bromine (water)

Allow Cl_2 or I_2

Allow O_2 if epoxide route used

M1



allow conseq equation to H_2, H_2O, HBr, HCl. HI and H_2SO_4

An epoxide is a feasible alternative that could score here and consequentially M3 and M4

M2

NaOH

***Or** KOH or other suitable strong alkali*

M3

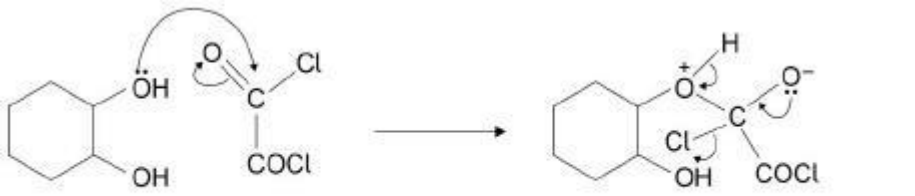
Allow this equation with molecular formulae

M4

(c) **M1** (nucleophilic)addition-elimination

Note lone pair required for M5

M1



M2 curly arrow from lp on O to C
M3 curly arrow from double bond to O
M4 for structure of intermediate
M5 for 3 curly arrows

M2
M3
M4
M5

(d) Less energy used **OR** Better yield

OR *reduces practical losses, simpler plant,*

M1

Less waste **OR** Less pollution

OR *maximises the use of raw materials in the process into useful products, saves resources*

M2

[13]

Q3.

D

ethanoyl chloride

[1]

Q4.

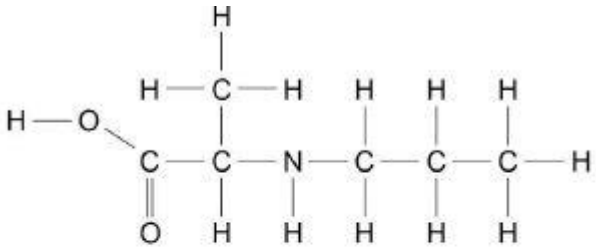
(a) One circled C atom only – The C attached to CH_3/C=O/ H and NH

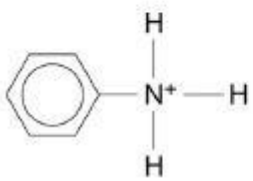
1

(b) Two ticks only for amine and amide

1

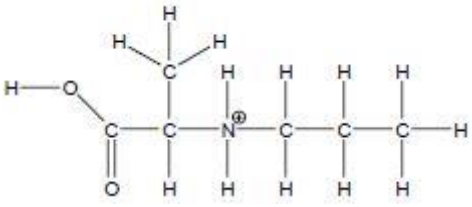
(c)





M1 *for choosing the correct bond to hydrolyse*
M2 *and* ***M3*** *for the correct structures of the products*

Allow protonated amino acid for M2



Allow $C_6H_5NH_3^+$ or + outside a square bracket

3

(d) **M1** Enzyme has an active site

1

M2
The G-Enantiomer / Enzyme has the correct stereo chemistry / stereospecific
Or
The G-Enantiomer / Enzyme has the complementary shape

For M2 allow opposite argument for F-Enantiomer

1

[7]

Q5.

(a) **M1** (Re)weigh the empty boat

1

M2 In order to calculate the (exact) mass of salicylic acid added to the reaction mixture

1

(b) 10 cm^3 measuring cylinder (if volume given – allow between 10 to 50 cm^3)
Or a 10 cm^3 pipette

Or burette / graduated pipette

Or 10 cm^3 syringe

1

(c) Corrosive

Allow skin burn / permanent eye damage
Ignore irritant / toxic

1

(d) LHS + $(CH_3CO)_2O$ RHS + CH_3COOH

1

(e) **M1** Amount salicylic acid = $^{6.01}/_{138}$ = 4.36×10^{-2} mol

Allow conseq from wrong mole ratio in (d)
Must show and state that ethanoic anhydride is in excess

1

M2 Mass $(CH_3CO)_2O$ = 10.5 × 1.08 = 11.34 g

1

M3 Amount $(CH_3CO)_2O$ = $^{11.34}/_{102}$ = 1.11×10^{-1} mol

For M4/M5 ecf from M1/M3

1

M4 $(CH_3CO)_2O$ is in excess

1

M5 Mass aspirin = M1 × 0.841 × 180 = 6.59 g

Allow 2 sf or more.

1

(f) **M1** Value lower

1

M2 Range of values

For M2 allow mpt not sharp or a larger range of melting points

1

(g) **M1** (Ethanol is flammable so) use a water bath to heat / do not use a Bunsen burner

Must give practical step, not just state hazard

1

M2 Heat to temp below bp (so ethanol does not boil away)

Allow use min vol solvent

1

(h) To remove any soluble impurities

Allow To avoid aspirin dissolving (small amount cold solvent used)

Allow To remove/(wash away) any ethanolic solution on the product.

1

(i) Pure product will have (larger) crystals / needle-like crystals / lighter in colour

Allow whiter, less grey, more crystalline, less powdery, shinier, single colour

Must be tied to pure product

Allow opposite points tied to the crude product

1

[16]

Q6.

(a) **M1** EQM amount A = 0.25 – 0.015 = 0.235 mol

Allow 0.24 mol for M1

1

M2 EQM amount B = 0.25 – (2 x 0.015) = 0.22 mol

1

(b) **M1** $K_c = \dfrac{[C]}{[A][B]^2}$

1

M2 $\dfrac{\frac{0.02}{0.35}}{\frac{0.30}{0.35} \times \left(\frac{0.25}{0.35}\right)^2}$

Correct insertion of numbers and use of volume

Allow ecf from their K_c

Scores M1 here (even if volume not used)

1

M3 = 0.13

Kc = 1.067 if vol not used Max 3

Kc = 7.63 if expression upside down Max 3

1

M4 Units $mol^{-2}\ dm^6$

Allow answers using cm^3 and then the corresponding units i.e. $1.31 \times 10^5\ mol^{-2}\ cm^6$

Allow conseq units to wrong K_c

1

(c) $[H_2O]$ / conc of water is (effectively) constant (because it it so much larger than the other concentrations)

1

(d) **M1** Initial amount $ClCH_2CHO = {}^{4.71}/_{78.5} = 0.06$ mol

Calculates initial mol

1

M2 EQM amount $ClCH_2CHO = (0.06 - x)$ mol

EQM amount $ClCH_2CH(OH)_2 = x$ mol

Sets up algebraic expressions for EQM mol of both

If no M2 can only score M3 and M5 conseq leads to 44.4 mol dm^{-3}

via $[ClCH_2CHO] = \frac{0.06}{0.05}$

1

M3 $37 = \dfrac{\frac{x}{V}}{\frac{(0.06-x)}{V}}$

Inserts into K

Does not need to show V as it cancels but allow expressions that do show V and subsequent calculations

1

M4 $37(0.06 - x) = x$

$2.22 = 38x$

$x = 0.058421$

Solve for x

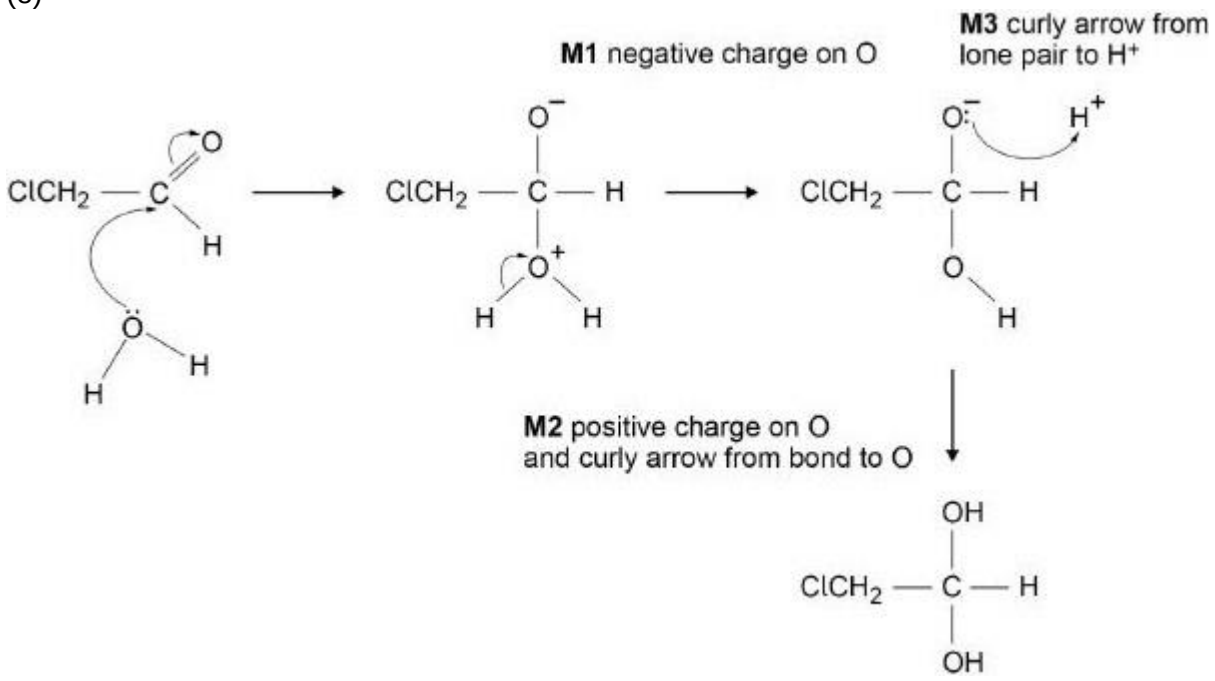
1

M5 $[ClCH_2CH(OH)_2] = \frac{0.058421}{0.05} = 1.17$ mol dm^{-3}

Calculate concentration

1

(e)



3

(f) **M1** C in C=O is less δ+ / less electron deficient

Allow converse

Ignore discussion in terms of C-Cl bond polarity

1

M2 Because CH_3 attached is electron donating Or

CH_3 has a (positive) inductive effect

1

M3 So higher E_a

*Allow for **M3** water less attracted to δ+C / electron deficient C / C in C=O*

(so lower collision frequency/ fewer collisions with correct orientation)

1

[18]

Q7.

B

[1]

Q8.

(a) Electrophilic substitution both words needed

Allow minor spelling errors e.g. electrophillic or subsitution

Ignore nitration

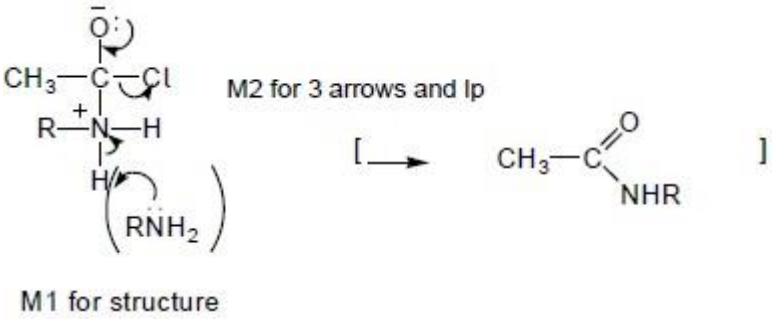
1

(b) + $3H_2$ ..... + $2H_2O$

Allow 6 [H]

1

(c)



***M1** for structure of ion including 2 charges (+ on N must be correct in both cases if drawn twice)*

***M2** for 3 arrows and lp on O - may be scored in two steps*

*Ignore use of RNH_2 to remove H^+ in **M2**, but penalise use of Cl^-*

2

(d) Corrosive **OR** forms strong acid/HCl (fumes) **OR** vulnerable to hydrolysis **OR** dangerous (to use)

*Allow anhydride is less corrosive **OR** does not form strong acid fumes **OR** less vulnerable to hydrolysis*

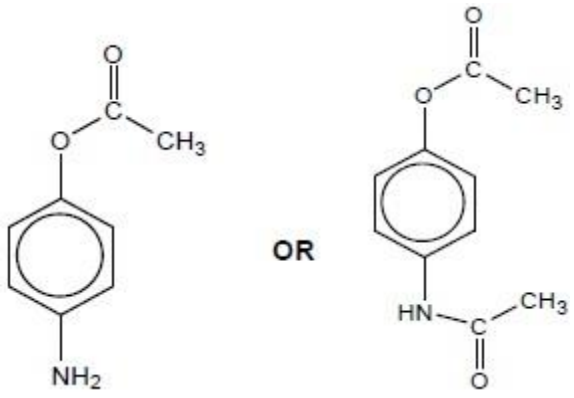
***OR** ethanoyl chloride is more expensive*

Allow reacts violently / extremely exothermic / extremely vigorous

Ignore toxic / harmful / hazardous

1

(e)



1

(f) + CH_3COONH_4 ..... + $2H_2O$

Allow CH_3COO^- / $CH_3CO_2^-$ and NH_4^+

Allow NH_4CH_3COO

1

(g) *Via moles*

M1 M_r paracetamol = 151(.0)

M1

M2 Amount paracetamol = 250 × 10^3 / 151.0 = 1655.6 mol
OR (250 × 10^3) / **M1**

(= amount hydroquinone used)

M2

M3 Mass hydroquinone = 1655.6 × 110.0 = 182119 g = 182 kg
OR correct answer to **M2** × 110.0 / 1000

M3

OR via mass
M1 *M_r paracetamol = 151(.0)*
So 110 g hydroquinone forms 151 g paracetamol
M2 *Mass hydroquinone needed 250 × 110 / 151.0*
OR *250 × 110 /* ***M1***
= 182 kg

Min 2sf
If Mr values used wrong way round can score ***M2***

[10]