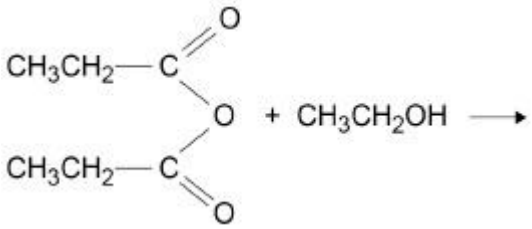
Q9.

This question is about esters including biodiesel.

(a) An ester is formed by the reaction of an acid anhydride with CH_3CH_2OH

Complete the equation. In your answer show clearly the structure of the ester.
Give the IUPAC name of the ester.

Equation



Name of ester _____

(3)

(b) In a reaction to form biodiesel, one mole of a vegetable oil reacts with an excess of methanol to form two moles of an ester with molecular formula $C_{19}H_{34}O_2$ and one mole of an ester with molecular formula $C_{19}H_{36}O_2$

Draw the structure of the vegetable oil showing clearly the ester links.

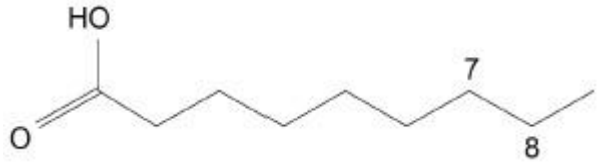
You should represent the hydrocarbon chains in the form C_xH_y where *x* and *y* are the actual numbers of carbon and hydrogen atoms.

(2)

(c) The compound $C_{19}H_{34}O_2$ is the methyl ester of Z,Z-octadeca-9,12-dienoic acid.

Part of the structure of the acid is shown.

Complete the skeletal formula to show the next part of the hydrocarbon chain to carbon atom number 14.
In your answer, show the Z stereochemistry around both C=C double bonds.



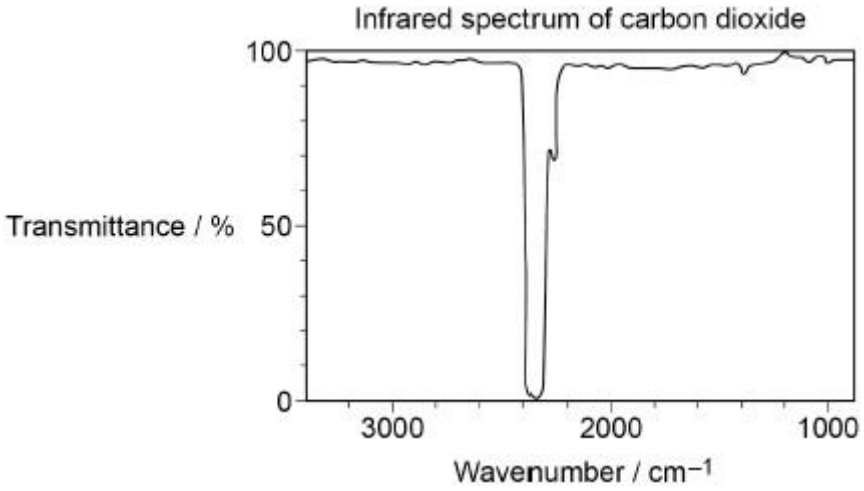
(2)

(d) Give an equation for the complete combustion of the ester $C_{19}H_{34}O_2$

_____

(1)

(e) Combustion of biodiesel produces greenhouse gases such as carbon dioxide that cause global warming.
Part of the infrared spectrum of carbon dioxide is shown in the diagram.



State how the infrared spectrum of carbon dioxide in the diagram above is **not** what you might predict from the data provided in **Table A** in the Data Booklet.

_____

_____

_____

(1)

(f) Explain how carbon dioxide causes global warming.

_____

_____

_____

_____

_____

_____

(2)

(Total 11 marks)

Q10.

A student is required to dry a liquid sample of pentanoic acid.

Which drying agent is suitable?

A Calcium oxide ⬭

B Calcium sulfate ⬭

C Potassium hydroxide ⬭

D Potassium carbonate ⬭

(Total 1 mark)

Q11.

Acyl chlorides are useful reagents in synthesis. They react with aromatic compounds and also with alcohols.

(a) CH_3CH_2COCl reacts with benzene in the presence of $AlCl_3$ in an electrophilic substitution reaction.

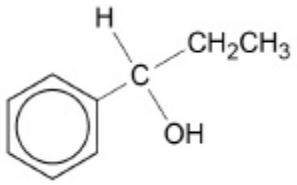
Give an equation for the reaction of CH_3CH_2COCl with $AlCl_3$ to form the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

Equation _____

Mechanism

(4)

(b) The organic product in **part (a)** can be converted into the alcohol shown.



Give the IUPAC name of the alcohol.
Give the reagent needed for this reaction and name the mechanism.

IUPAC name _____

Reagent _____

Name of mechanism _____

(3)

(c) The alcohol shown in **part (b)** reacts with ethanoyl chloride to form an ester.

Describe what would be observed when the alcohol reacts with ethanoyl chloride.
Name the mechanism for the reaction to form the ester.
Draw the structure of the ester.

Observation _____

_____

Name of mechanism _____

Structure of ester

(3)
(Total 10 marks)

Q12.

Use the Data Booklet to help you answer this question.

This question is about amino acids and peptide (amide) links.

(a) Draw the structure of the zwitterion formed by phenylalanine.

(1)

(b) Draw the structure of serine at high pH.

(1)

(c) Draw the structures of both dipeptides formed when phenylalanine reacts with serine.

In each structure show all the atoms and bonds in the amide link.

(2)

(d) An amide link is also formed when an acyl chloride reacts with a primary amine.

Name and outline a mechanism for the reaction between CH_3CH_2COCl and $CH_3CH_2NH_2$

Give the IUPAC name of the organic product.

Name of mechanism _____

Mechanism

IUPAC name of organic product _____

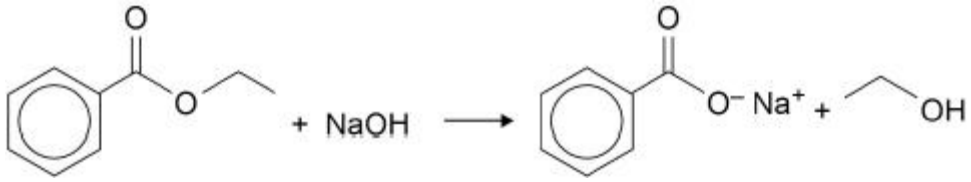
(6)

(Total 10 marks)

Q13.

Benzoic acid can be prepared from ethyl benzoate.

Ethyl benzoate is first hydrolysed in alkaline conditions as shown:



A student used the following method.

Add 5.0 cm^3 of ethyl benzoate (density = 1.05 g cm^{-3}, M_r = 150) to 30.0 cm^3 of aqueous 2 mol dm^{-3} sodium hydroxide in a round-bottomed flask.

Add a few anti-bumping granules and attach a condenser to the flask. Heat the mixture under reflux for half an hour. Allow the mixture to cool to room temperature.

Pour 50.0 cm^3 of 2 mol dm^{-3} hydrochloric acid into the cooled mixture.

Filter off the precipitate of benzoic acid under reduced pressure.

(a) Suggest how the anti-bumping granules prevent bumping during reflux.

_____

_____

_____

(1)

(b) Show, by calculation, that an excess of sodium hydroxide is used in this reaction.

(2)

(c) Suggest why an excess of sodium hydroxide is used.

_____

_____

(1)

(d) Suggest why an electric heater is used rather than a Bunsen burner in this hydrolysis.

_____

_____

(1)

(e) State why reflux is used in this hydrolysis.

_____

_____

(1)

(f) Write an equation for the reaction between sodium benzoate and hydrochloric acid.

_____

(1)

(g) Suggest why sodium benzoate is soluble in cold water but benzoic acid is insoluble in cold water.

_____

_____

_____

_____

_____

(2)

(h) After the solid benzoic acid has been filtered off, it can be purified.

Describe the method that the student should use to purify the benzoic acid.

(6)

(i) In a similar experiment, another student used 0.040 mol of ethyl benzoate and obtained 5.12 g of benzoic acid.

Calculate the percentage yield of benzoic acid.

Suggest why the yield is not 100%.

Percentage yield _____ %

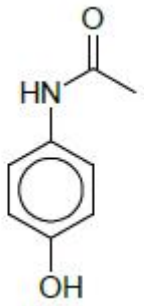
Suggestion _____

(3)

(Total 18 marks)

Q14.

Paracetamol is a common analgesic used for the relief of pain. It has the structure shown.



The melting point of paracetamol is 170 °C.
Paracetamol can be prepared from the reaction between 4-aminophenol ($HOC_6H_4NH_2$) and ethanoyl chloride.

(a) Write an equation for this reaction.

_____

(1)

(b) Name and outline the mechanism for this reaction. Use RNH_2 to represent 4–aminophenol.

Name of mechanism _____

Mechanism

(5)

(c) The paracetamol formed in this reaction is impure. It contains both soluble and insoluble impurities that must be removed by recrystallisation.

The properties of a suitable solvent for recrystallisation are shown.

- The paracetamol should dissolve when the solvent is hot but be almost insoluble when the solvent is cold.
- The impurities should either be insoluble in the solvent at all temperatures or soluble even in cold solvent.
- When a hot saturated solution of the paracetamol is cooled, as much product as possible should crystallise out, leaving soluble impurities in the solution.

A solvent has been suggested for this recrystallisation. It is a flammable liquid with a boiling point of 80 °C.

Outline how you would carry out an investigation to show that this solvent is suitable for the recrystallisation of the impure paracetamol. You should include brief practical details of how you would carry out your investigation.

You are **not** required to describe the full recrystallisation procedure.

Explain how you would check that a recrystallisation process had been effective at producing a pure sample of paracetamol.

(6)

(d) When paracetamol is prepared by reacting an excess of 4-aminophenol with ethanoyl chloride, the expected percentage yield of impure paracetamol is 65%.

An expert practical chemist might expect to lose, at most, a further 20% of the impure product during recrystallisation.

A student started with 3.87 g of ethanoyl chloride.

After preparation of impure paracetamol followed by recrystallisation, the student actually obtained 4.07 g of pure paracetamol.

Calculate the mass of impure paracetamol expected from this experiment, based on a 65% yield.

Use your answer and the actual mass of pure paracetamol obtained, to comment on the statement that “the student has demonstrated expert practical skills”.

(4)

(e) Suggest why the student should **not** use this sample of paracetamol for the purposes of pain relief.

(1)

(f) Suggest **two** reasons why, in an industrial situation, ethanoic anhydride would be preferred to ethanoyl chloride in the production of paracetamol.

1.

2.

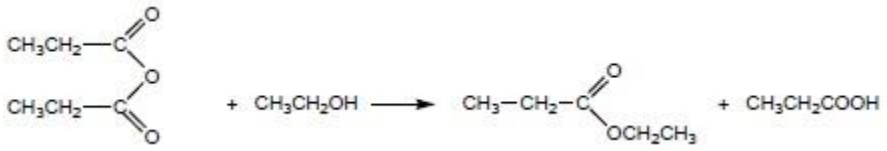
(2)

(Total 19 marks)

Mark Scheme

Q9.

(a)



Ethyl propanoate only

M1 *Structure of ester (allow $C_2H_5CO_2C_2H_5$)*

1

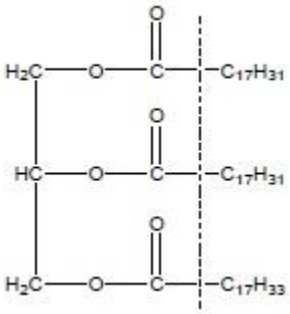
M2 *propanoic acid formula (allow $C_2H_5CO_2H$) and correctly balanced equation*

1

M3 *Ethyl propanoate only*

1

(b)



M1 for all except $C_{17}H_{3x}$ (i.e. all to the left of the dotted line)

Allow $–O_2C–$, $–OOC–$, $–OCO–$

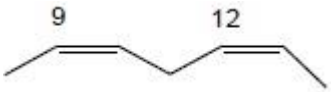
Not $–CO_2–$, $–COO–$

1

M2 for two $C_{17}H_{31}$ and one $C_{17}H_{33}$ in any order top to bottom

1

(c)



M1 for skeleton

1

M2 for both Z correct
Independent marks

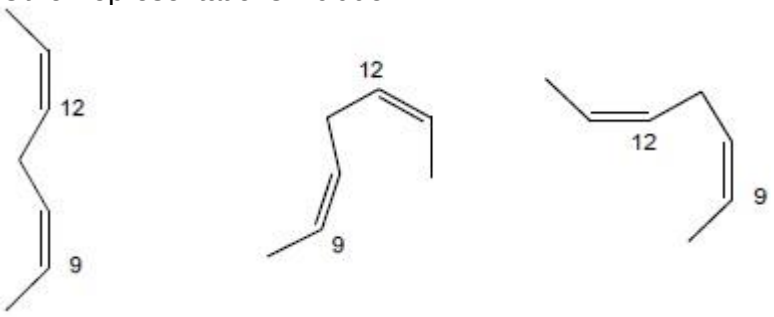
1

C9 – C14 shown with double bonds in the correct place

Ignore structure beyond carbon 14

*If hydrogens shown or not skeletal can only score **M2***

Other representations include



(d) $C_{19}H_{34}O_2 + 26½\ O_2 \longrightarrow 19\ CO_2 + 17\ H_2O$

Allow 53/2 or all doubled

1

(e) Absorption in spectrum at 2350 cm^{-1} does not correspond to data booklet value of 1680 – 1750 cm^{-1} or for C=O bonds in organic compounds)

Allow would expect a peak at 1680 – 1750 cm^{-1}

1

(f) C=O Bonds in CO_2 absorb infrared radiation (of 2350 cm^{-1})

1

IR radiation emitted by the earth does not escape (from the atmosphere)
OR
This energy is transferred to other molecules in the atmosphere by collisions (so all atmosphere is warmed)

Ignore IR reflected

1

[11]

Q10.

B

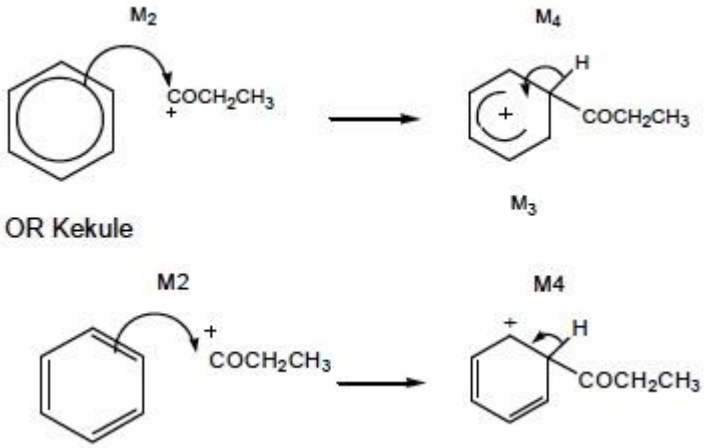
[1]

Q11.

(a) $AlCl_3 + CH_3CH_2COCl \longrightarrow CH_3CH_2{-}\overset{+}{C}{=}O + AlCl_4^-$

Allow + on C or O in equation –
But must be on C in mechanism

M1



M2 Arrow from inside hexagon to C or + on C

1

M3 Structure of intermediate

- *horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6)*

1

M4 Arrow from bond into hexagon (Unless Kekule)

- *Can allow M4 arrow independent of wrong M3 structure*
- *+ on H in intermediate loses M3 not M4*
- *Ignore Cl^- and $AlCl_4^-$*

- used in M4

1

(b) Either...

1-phenylpropan-1-ol

1

$NaBH_4$ / $LiAlH_4$

1

Nucleophilic addition

1

Or...

1-phenylpropan-1-ol

1

H_2 with Ni/Pd/Pt

1

Addition/hydrogenation

1

Both numbers needed for names

Ignore solvents

(c) Misty fumes / steamy fumes

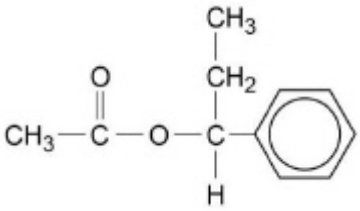
Allow sweet/fruity smell / white fumes

Not smoke

1

(Nucleophilic) addition-elimination

1

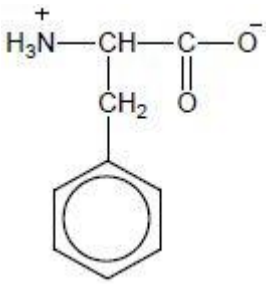


1

[10]

Q12.

(a)

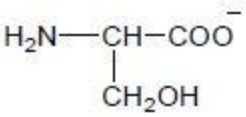


Allow $-CO_2^-$

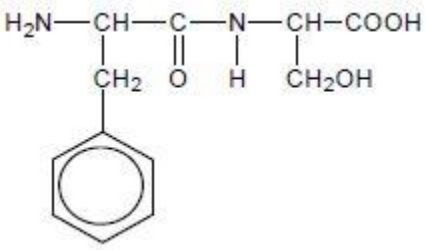
Allow $^+H_3N-$ and NH_3^+-

1

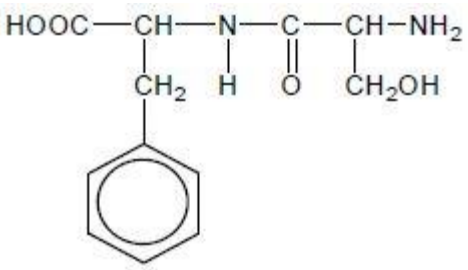
(b)



(c)



1



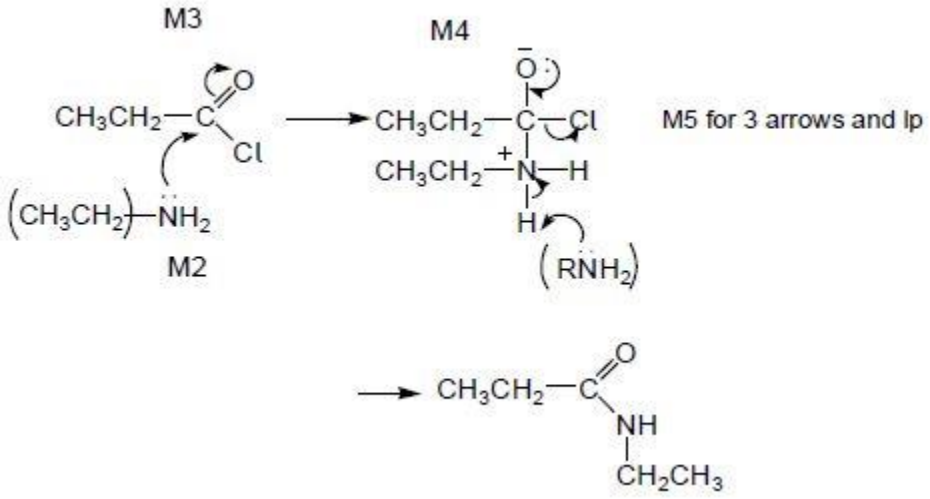
1

If same wrong amino acid twice – max 1

(d) (nucleophilic) addition-elimination

Not electrophilic addition-elimination.

M1



M2 for arrow from lp on N to C

(or to space half way between N and C)

Ignore δ+ and δ− unless wrong

M3 for arrow from C=O bond to O

Not score M3 as an independent first step, but can allow M2 for attack on C+ produced

If Cl lost at this stage, Max 1 for mechanism for M2

M4 for structure of ion including 2 charges

(+ on N must be correct in both cases if drawn twice)

M5 for 3 arrows and lp on O

- may be scored in two steps

Ignore use of RNH_2 to remove H^+ in M5, but penalise use of Cl^-

M2-5

N-ethylpropanamide

M6

[10]

Q13.

(a) allows smaller <u>bubbles</u> to form / prevents the formation of (very) large <u>bubbles</u>

ALLOW provides large surface area for <u>bubbles</u> to form on

IGNORE 'air'

NOT no bubbles form / prevents bubbles forming

1

(b) (Mass of ester = 1.05 × 5.0 = 5.25g)
amount of ester = 5.25 / 150.0 = 0.0350 mol

1

amount of NaOH = 30 × 2 / 1000 = 0.06 mol

1

OR

(Mass of ester = 1.05 × 5.0 = 5.25g)
amount of ester = 5.25 / 150.0 = 0.0350 mol

1

Vol of 0.035 mol of NaOH = (0.035/2) × 1000 = 17.5 cm^3
(so 30 cm^3 used is an excess)

1

OR

amount of NaOH = 30 × 2 / 1000 = 0.06 mol

1

0.06 mol of ester = 9 g = 8.57 cm^3
(only 5 cm^3 used so NaOH in excess)

1

Mark independently

Max 2

(c) To ensure that the ester is completely hydrolysed / to ensure all the ester reacts

ALLOW to ensure the other reagent has completely reacted

1

(d) Many organic compounds / the ester / ethanol are flammable

ALLOW prevent ignition of any flammable vapours formed

1

(e) Reflux allows reactant vapours (of volatile organic compounds) to be returned to the reaction mixture / does not allow any reactant vapour to escape

IGNORE reference to products

1

(f) $C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl$

Allow ionic equation.

ALLOW molecular formulae ($C_7H_5O_2Na$ and $C_7H_6O_2$)

ALLOW skeletal benzene ring

1

(g) Sodium benzoate soluble because it is ionic

IGNORE polar

1

Benzoic acid insoluble because: despite the polarity of the COOH group / ability of COOH to form H-bonds, the benzene ring is non-polar.

ALLOW 'part of molecule' or 'one end' for COOH

1

(h) Dissolve crude product in <u>hot</u> solvent/water

ALLOW ethanol

If no M1 max = 4

1

of minimum volume

ALLOW reference to saturated soln as alternative to 'min vol'

1

Filter (hot to remove insoluble impurities)

IGNORE use of Buchner funnel here

1

Cool to recrystallise

apply list principle for each additional process in an incorrect method but IGNORE additional m.pt determination

1

Filter under reduced pressure / with Buchner/Hirsch apparatus

1

wash (with cold solvent) **and** dry

1

(i) 5.12 / 122 (= 0.042 mol)

method mark

1

(0.042/0.04) × 100 = 105 %

ecf for M1/0.04

or calculation that 0.04 mol of benzoic = 4.88 g (M1) so

% yield = (5.12/4.88) × 100 = 105%

1

Product not dried / impurities present in product

Only allow M3 if M2>100%

1

[18]

Q14.

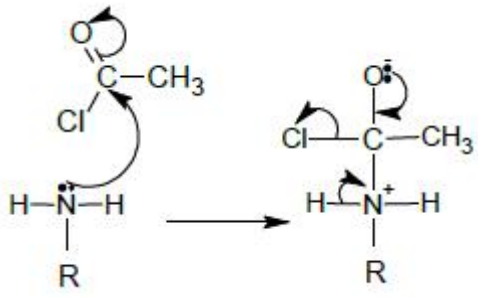
(a) $2HO–C_6H_4–NH_2 + CH_3COCl \longrightarrow HO–C_6H_4–NHCOCH_3 + HO\text{-}C_6H_4\text{-}NH_3^+Cl^-$

$HO–C_6H_4–NH_2 + CH_3COCl \longrightarrow HO–C_6H_4–NHCOCH_3 + HCl$

1

(b) (Nucleophilic) Addition-elimination.

1



M2 = Arrow from lone pair on N to carbon in C=O.

1

M3 = Arrow from the bond in CO to the O.

1

M3 = Correct intermediate with + on N and − on O.

1

M4 = Three arrows and lone pair.

1

(c) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

Level 3

Outlines a workable process with clear decision-making process. Gives a method for melting point determination with detailed reference to the melting point of 170 ± 2 °C.

5-6 marks

Level 2

Outlines a workable process with some indication of decision-making. Gives a method for melting point determination without detailed reference to the melting point of 170 ± 2 °C.

3-4 marks

Level 1

Partially outlines a potentially workable process. Suggests need for melting point determination.

1-2 marks

Level 0

Insufficient correct chemistry to warrant a mark.

0 marks

Indicative Chemistry content

- *Place a small amount of pure paracetamol in a test-tube.*
- *Add small volume (0.5–1.0 cm^3) of possible solvent*
- *Shake/stir.*
- *If paracetamol dissolves then solvent unsuitable.*
- *Heat (with suitable awareness of flammability and boiling point; e.g. hot − not boiling − water bath).*
- *If paracetamol does not dissolve = unsuitable.*
- *If paracetamol dissolves partially try adding more solvent.*
- *If/when completely dissolved place test-tube in ice-water bath.*
- *If crystals form = suitable.*
- *Effectiveness determined by measuring melting point.*
- *Purity indicated by melting point being sharp and close to 170 °C.*

6

(d) Amount of ethanoyl chloride = 3.87 / 78.5 = 0.0493 mol

1

(Theoretical mass of paracetamol = 0.0493 × 151 = 7.44 g)
Mass expected = (65/100) × 7.44 = 4.84 g

1

Loss in mass on recrystallisation = 4.84 − 4.07 = 0.77

1

Percentage loss in mass = (0.77 / 4.84) × 100 = 15.9 %
This suggests that the student has demonstrated expert practical skills as less than 20 % loss during recrystallisation.

Allow *comment that it is unlikely student would be better than expert chemist so final product may not be dry thus increasing apparent mass obtained.*

1

(e) There may still be small amounts of impurities.

1

(f) Any **two** from:

- less exothermic reaction
- easier to control
- dangerous gas not evolved
- ethanoic anhydride is a cheaper or more easily recycled reagent.

2

[19]