Q1. (a) Write an equation for the formation of methyl propanoate, $CH_3CH_2COOCH_3$, from methanol and propanoic acid.

_____

(1)

(b) Name and outline a mechanism for the reaction between methanol and propanoyl chloride to form methyl propanoate.

Name of mechanism _____

Mechanism

(5)

(c) Propanoic anhydride could be used instead of propanoyl chloride in the preparation of methyl propanoate from methanol. Draw the structure of propanoic anhydride.

(1)

(d) (i) Give **one** advantage of the use of propanoyl chloride instead of propanoic acid in the laboratory preparation of methyl propanoate from methanol.

_____

_____

(ii) Give **one** advantage of the use of propanoic anhydride instead of propanoyl chloride in the industrial manufacture of methyl propanoate from methanol.

_____

_____

(2)

(e) An ester contains a benzene ring. The mass spectrum of this ester shows a molecular ion peak at *m/z* = 136.

(i) Deduce the molecular formula of this ester.

_____

_____

_____

(ii) Draw **two** possible structures for this ester.

(3)
(Total 12 marks)

Q2. Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

(a) Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

(4)

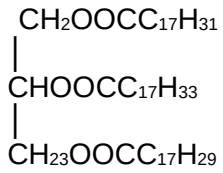
(b) Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

(3)

(c) Name and outline a mechanism for the reaction of CH_3COCl with CH_3OH to form an ester.

(d) The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.



(3)

(e) Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradeable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

(4)

(Total 19 marks)

Q3. Aldehydes can be prepared from acyl chlorides.

State how an aldehyde could be tested to show whether it is contaminated with traces of unreacted acyl chloride.
State what you would observe.

Test _____

Observation _____

_____

(Total 2 marks)

Q4. The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of CH_3CH_2COCl and of $CH_3CH_2CH_2Cl$ with ammonia.

(a) For the reaction of CH_3CH_2COCl with ammonia, name and outline the mechanism and name the organic product.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

(6)

(b) For the reaction of $CH_3CH_2CH_2Cl$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

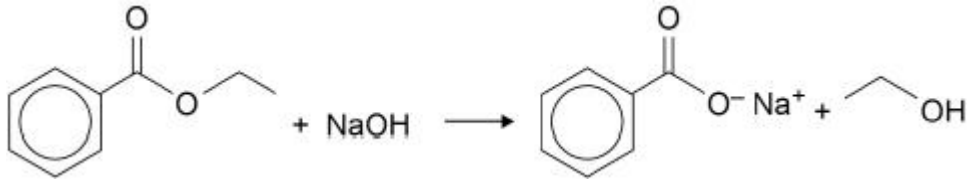
(6)

(c) Suggest **one** reason why chlorobenzene (C_6H_5Cl) does **not** react with ammonia under normal conditions.

(1)

(Total 13 marks)

Q5. 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 _____

(total 18 marks)

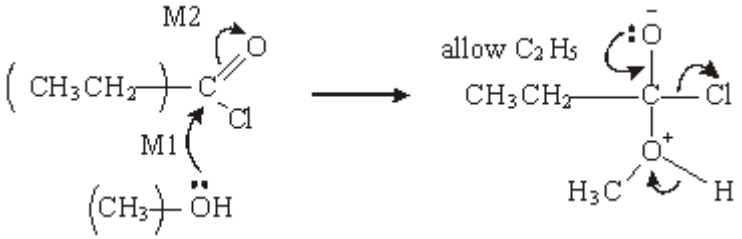
Q1.

(a) $CH_3OH + CH_3CH_2COOH \rightarrow CH_3CH_2COOCH_3 + H_2O$

1

(b) (nucleophilic) addition–elimination NOT acylation

1



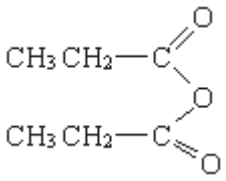
ignore use of Cl^- to remove H^+

M3 for structure

M4 for 3 arrows and lone pair

4

(c)



allow C_2H_5 and $–CO_2–$

allow $CH_3CH_2COOCOCH_2CH_3$

or *$(CH_3CH_2CO)_2O$*

1

(d) (i) faster/not reversible/bigger yield/purer product/no(acid) (catalyst) required

1

(ii) anhydride less easily hydrolysed or reaction less violent/exothermic
no (corrosive) (HCl) fumes formed or safer or less toxic/dangerous
expense of acid chloride or anhydride cheaper

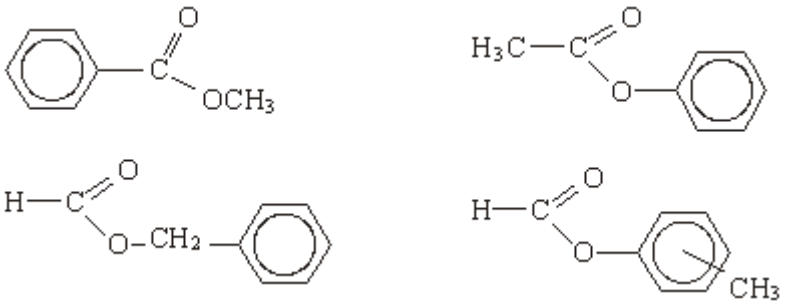
any one

1

(e) (i) $C_8H_8O_2$

1

(ii) **any** two **from**



Allow –CO_2– allow C_6H_5

2

[12]

Q2.

(a) **M1** $CH_3CH_2CH_2COOH$

not C_3H_7COOH

1

M2 CH_3CH_2OH or C_2H_5OH

1

M3 $CH_3CH_2CH_2COOCH_2CH_3 + H_2O$

allow $C_3H_7COOC_2H_5$

penalise M3 for wrong products and unbalanced equation

1

M4 H_2SO_4 or HCl or H_3PO_4 conc or dil or neither

not HNO_3

1

(b) **M1** $CH_3CH_2CH_2CH_2OH$

1

not C_4H_9OH

M2 $(CH_3CO)_2O$

1

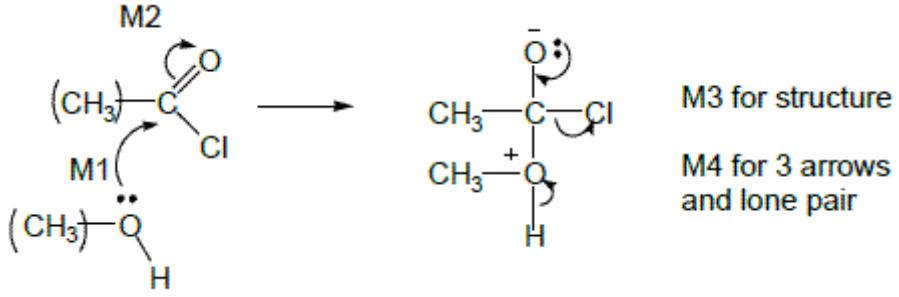
M3 → $CH_3COOCH_2CH_2CH_2CH_3 + CH_3COOH$

allow $CH_3COOC_4H_9$

penalise M3 for wrong products and unbalanced equation

1

(c) (nucleophilic) addition-elimination



not acylation alone

M2 not allowed indep of M1 but allow M1 for correct attack

on C+

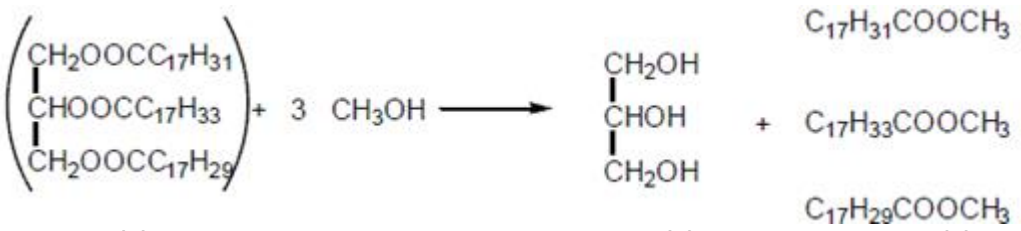
+C=O loses M2

only allow M4 after correct or v close M3

ignore Cl^- removing H^+

5

(d)



(1) (1) (1)

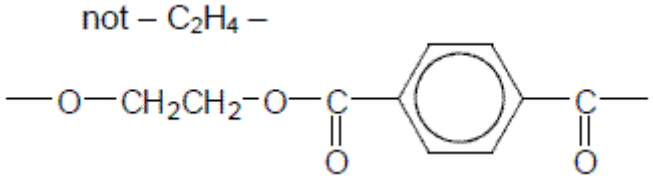
ignore errors in initial triester

First mark for $3CH_3OH$

Third mark for all three esters

3

(e)



First mark for correct ester link second mark for the rest including trailing bonds

If ester link wrong, lose second mark also

2

Adv reduces landfill
saves raw materials
lower cost for recycling than making from scratch
reduces CO_2 emissions by not being incinerated

not allow cost without qualification

ignore energy uses

1

Disad difficulty/cost of collecting/sorting/processing
product not suitable for original purpose, easily contaminated

not allow cost without qualification

ignore energy uses

1

[19]

Q3.

Test silver nitrate (solution) **(M1)**

Allow an alternative soluble silver salt eg fluoride, sulfate.

Do not allow 'silver ions' but can access second mark.

Incorrect formula loses this mark but can access second mark.

*Do not allow 'silver' or an insoluble silver salt and **cannot***

access second mark.

Ignore references to acidification of the silver nitrate.

If an acid is specified it should be nitric acid, but allow sulfuric acid in this case as there are no metal ions present.

If hydrochloric acid is used, CE = 0 / 2.

Do not allow 'add water'.

1

Observation white precipitate **(M2)**

Ignore 'cloudy'.

Do not allow 'white fumes' or 'effervescence'.

Do not allow this mark if test reagent is incorrect or missing.

*Allow named indicator paper or named indicator solution for **M1**.*

*Allow correct colour change for **M2**.*

1

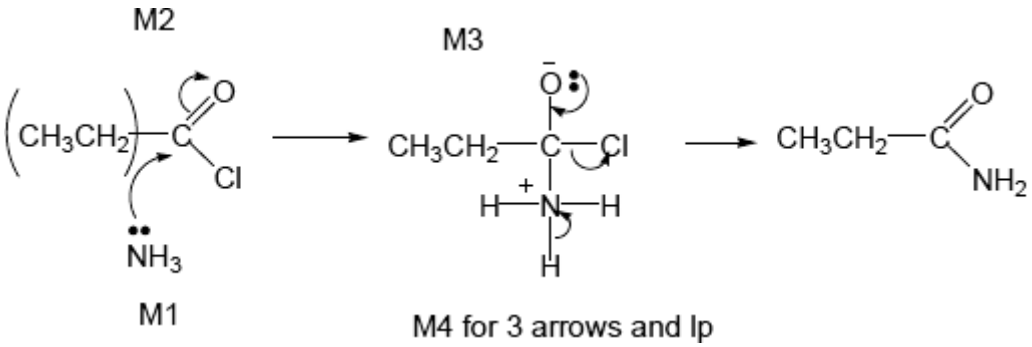
[2]

Q4.

(a) (Nucleophilic) addition-elimination

- *Minus sign on NH_3 loses M1(but not M4 also)*
- *M2 not allowed independent of M1, but*

1



- *allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- ***If Cl lost with C=O breaking, max1 for M1***
- ***M3** for correct structure with charges but lp on O is part of **M4***
- *only allow **M4** after correct/very close **M3***
- *For **M4**, ignore NH_3 removing H^+ but lose **M4** for Cl^- removing H^+ in mechanism,*
- *but ignore HCl shown as a product*

4

propanamide (Ignore -1-)

penalise other numbers

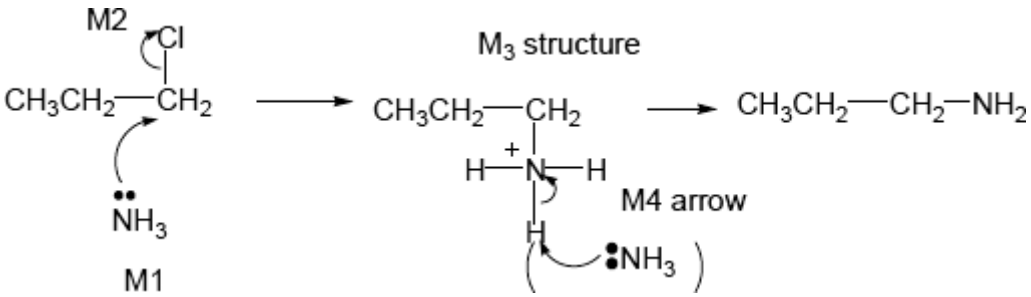
penalise propaneamide and N-propanamide

1

(b) Nucleophilic substitution

- *Minus sign on NH_3 loses M1 (not M4 also)*
- *+ rather than δ+ on C=O loses M2*

1



- *ALLOW SN1 so allow M2 for loss of Cl^- before attack of NH_3 on C+ for M1*
- *only allow M4 after correct/very close M3*
- *For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism,*

Propylamine (ignore number 1)

- *but ignore HCl shown as a product*

4

or propan-1-amine or 1-aminopropane (number 1 needed)

penalise other numbers

allow 1-propanamine

1

(c) electron rich ring or benzene or pi cloud repels nucleophile/ammonia

Allow

- *C–Cl bond is short/stronger than in haloalkane*
- *C–Cl is less polar than in haloalkane*
- *resonance stabilisation between ring and Cl*

1

[13]

Q5.

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

ALLOW provides large surface area for bubbles 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]