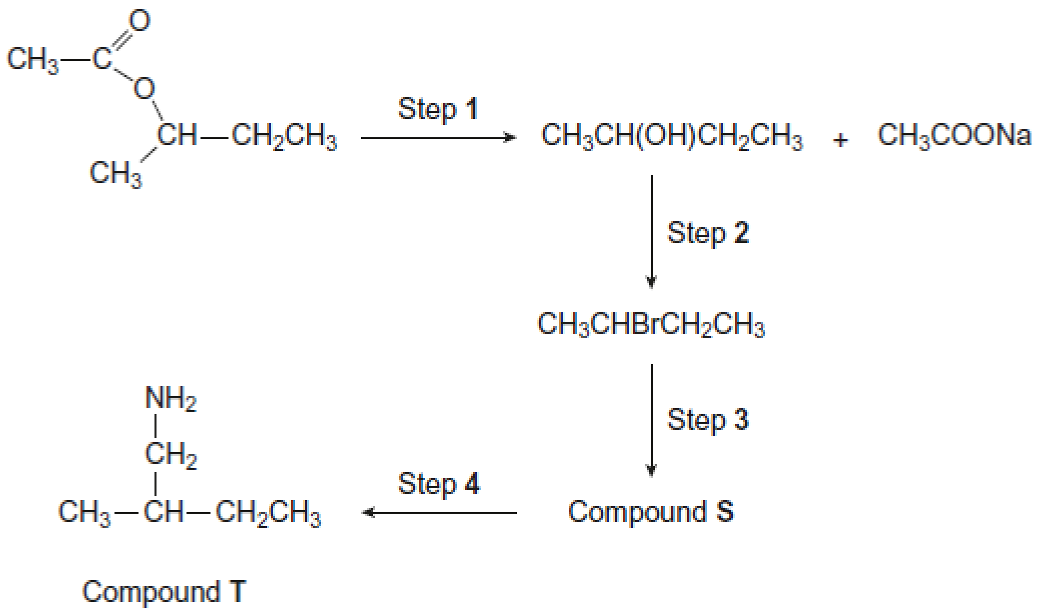
Q11.

A four-step synthesis of compound **T** is shown.



(a) Give the reagent and conditions for Step **1**.
State how you could obtain a sample of the alcohol from the reaction mixture formed in Step **1**.

(3)

(b) Draw the structure of compound **S**.
For each of Steps **3** and **4**, give a reagent and one condition, other than heat.

(5)

(Total 8 marks)

Q12.

Esters are used as raw materials in the production of soaps and biodiesel.

(a) A student prepared an ester by two different methods.

Method **1** alcohol + acid anhydride

Method **2** alcohol + acyl chloride

(i) An ester was prepared using method **1**, by reacting $(CH_3)_2CHOH$ with $(CH_3CO)_2O$

Write an equation for this reaction and give the IUPAC name of the ester formed.

Equation

____

IUPAC name of the ester ____

(2)

(ii) The same ester was prepared using method **2** by reacting $(CH_3)_2CHOH$ with CH_3COCl

Outline a mechanism for this reaction.

(4)

(b) The ester shown occurs in vegetable oils.
It can be hydrolysed to make soap and can also be used to produce biodiesel.

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

(i) Write an equation for the reaction of this ester with sodium hydroxide to form soap.

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

____

(2)

(ii) Give the formula of the biodiesel molecule with the highest M_r that can be produced by reaction of this ester with methanol.

____

(1)

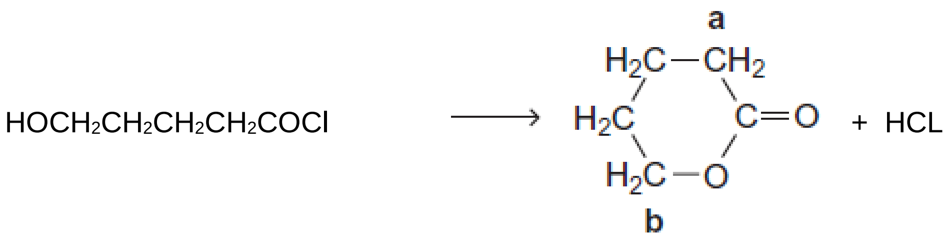
(Total 9 marks)

Q13.

This question is about some isomers of $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



H

(i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

(7)

(ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in part (i).

Draw the repeating unit of the polyester and name the type of polymerisation involved.

___

___

___

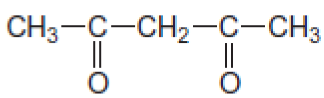
___

___

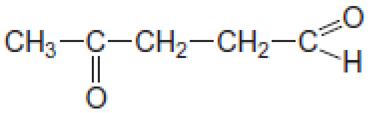
(2)

(b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ¹H n.m.r. spectrum of each compound.



J



K

___

___

___

___

___

___

___

___

(5)

(c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^1H n.m.r. spectrum.

(5)
(Total 19 marks)

Q14.

Esters are produced by the reaction of alcohols with other esters and by the reaction of alcohols with carboxylic acids.

(a) The esters which make up biodiesel are produced industrially from the esters in vegetable oils.

(i) Complete the equation for this formation of biodiesel.

$$\begin{array}{l} CH_2OOCC_{17}H_{35} \\ | \\ CHOOCC_{17}H_{31} \\ | \\ CH_2OOCC_{17}H_{29} \end{array} + \_\_\_\_\_\_\_\_\_\_ \rightleftharpoons \begin{array}{l} C_{17}H_{35}COOCH_3 \\ C_{17}H_{31}COOCH_3 \\ C_{17}H_{29}COOCH_3 \end{array} + \_\_\_\_\_\_\_\_\_\_$$

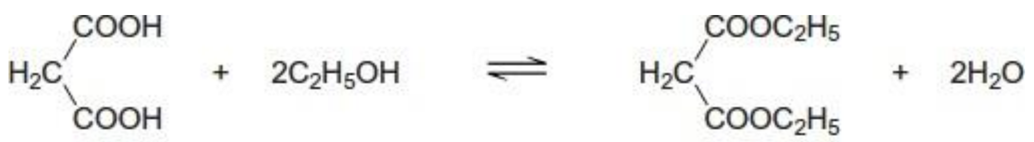
(2)

(ii) Write an equation for the complete combustion of $C_{17}H_{35}COOCH_3$.

____

(2)

(b) The ester commonly known as diethyl malonate (**DEM**) occurs in strawberries and grapes. It can be prepared from acid **A** according to the following equilibrium.



A **DEM**

(i) A mixture of 2.50 mol of **A** and 10.0 mol of ethanol was left to reach equilibrium in an inert solvent in the presence of a small amount of concentrated sulfuric acid. The equilibrium mixture formed contained 1.80 mol of **DEM** in a total volume, V dm^3, of solution.

Calculate the amount (in moles) of **A**, of ethanol and of water in this equilibrium mixture.

Moles of **A** ____

Moles of ethanol ____

Moles of water ____

(3)

(ii) The total volume of the mixture in part (b)(i) was doubled by the addition of more of the inert solvent.

State and explain the effect of this addition on the equilibrium yield of **DEM**.

Effect ____

Explanation ____

____

(2)

(iii) Using **A** to represent the acid and **DEM** to represent the ester, write an expression for the equilibrium constant K_c for the reaction.

____

____

(1)

(iv) In a second experiment, the equilibrium mixture was found to contain 0.85 mol of **A**, 7.2 mol of ethanol, 2.1 mol of **DEM** and 3.4 mol of water.

Calculate a value of K_c for the reaction and deduce its units.

Calculation ____

____

____

____

____

____

____

____

Units ____

____

(3)

(Total 13 marks)

Q15.

Salicylic acid, $C_6H_4(OH)COOH$, reacts with magnesium to produce magnesium salicylate and hydrogen.

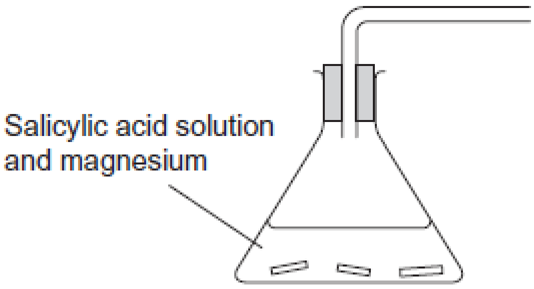
(a) Complete the equation for this reaction.

$C_6H_4(OH)COOH$

(1)

(b) In an alternative method for determining percentage purity, a student reacted a solution of salicylic acid with an excess of magnesium and collected the hydrogen gas that was released.

Complete the diagram below to show an apparatus that could be used to collect and measure the volume of hydrogen gas produced.



(1)

(Total 2 marks)

Q16.

The slowing down of chemical processes is important in food storage. Over time, fats may become rancid. This involves the formation of compounds that have unpleasant odours and flavours within the food.
Hydrolysis of fats is one way in which rancid flavours are formed. Fats break down to long-chain carboxylic (fatty) acids and glycerol.

(a) Complete the right-hand side of the equation below to show how hydrolysis affects the molecule of fat shown.

$CH_3(CH_2)_{14}COOCH_2$
|
$CH_3(CH_2)_{14}COOCH$
|
$CH_3(CH_2)_{14}COOCH_2$ + $3H_2O \rightarrow$ 3 .... + ...

(2)

(b) Other than by cooling, suggest **one** method that would decrease the rate of hydrolysis of fats.

____

____

____

(1)

(c) Food can also acquire unpleasant flavours when the fatty acids, produced by hydrolysis of fats, are oxidised by air. This oxidation occurs by a free-radical mechanism.
Chemicals called anti-oxidants can be added to food to slow down the oxidation.
Suggest why anti-oxidants are **not** regarded as catalysts.

____

____

____

____

(2)

(d) A student investigated the extent of hydrolysis in an old sample of the fat in part (a).
The carboxylic acid extracted from a 2.78 g sample of this fat (M_r = 806.0) reacted with 24.5 cm^3 of a 0.150 mol dm^{-3} solution of NaOH.
Calculate the percentage of the fat that had hydrolysed.
Show your working.

____

____

____

____

____

____

____

____

(4)

(Total 9 marks)

Q17.

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)

Mark Scheme

Q11.

(a) M1 NaOH

Only score M2 if M1 gained, but mark on from hydroxide. Mention of acid loses M1 & M2

1

M2 Aqueous/(warm)

Ignore alcoholic / conc / dil.

1

M3 (Fractional) distillation or described

Not just evaporation; not reflux

Allow chromatography

1

(b) M1 S is $CH_3CH(CN)CH_2CH_3$

Allow without brackets

1

Step 3

M2 KCN (mark on from CN^-)

Not HCN, not KCN with acid

1

M3 Alcoholic / (aqueous)

Allow ethanolic

Can only score M3 if M2 gained

1

Step 4

M4 H_2

$LiAlH_4$

Na

Can only score M5 if M4 gained

1

M5 Ni or Pt or Pd

Ethoxyethane or ether

$LiAlH_4$ with acid loses both M4 and M5

Ignore 'followed by acid'

Na

Ethanol

NOT $NaBH_4$ OR Sn/HCl

Penalise other extras as list
Ignore pressure or temperature

1

[8]

Q12.

(a) (i) $(CH_3)_2CHOH + (CH_3CO)_2O \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$

__Allow__ $CH_3CO_2CH(CH_3)_2$ and CH_3CO_2H
Ignore $(CH_3)_2$ −C in equation

1

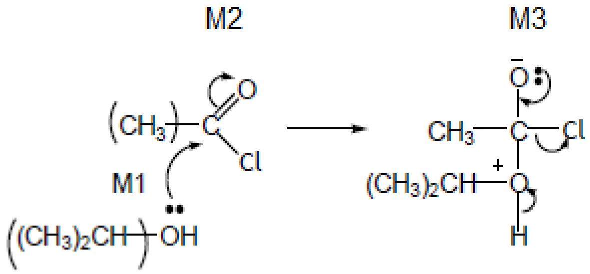
(1)-methylethyl ethanoate OR

Propan-2-yl ethanoate

Ignore extra or missing spaces, commas or hyphens

1

(ii)



M4 for 3 arrows and lp

NO Mark for name of mechanism

M1 for lone pair on O and arrow to C or to mid-point of space between O and C

M2 for arrow from C=O bond to O

- *M2 not allowed independent of M1, but 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 <u>with charges</u> (penalise wrong alcohol here) but lone pair on O is part of M4

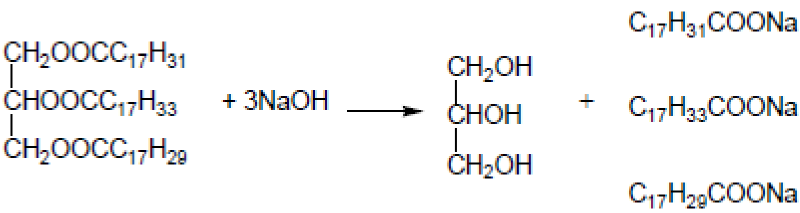
Penalise $(CH_3)_2$ −C in M3

M4 for lone pair on O and three arrows

- *Only allow M4 after correct / very close M3*
- *M4 can be gained over more than one structure*
- *Ignore Cl− removing H^+*

4

(b) (i)



Penalise covalent Na e.g. -O-Na

LHS 1
RHS 1

(ii) $C_{17}H_{33}COOCH_3$

Allow $C_{19}H_{36}O_2$

1

[9]

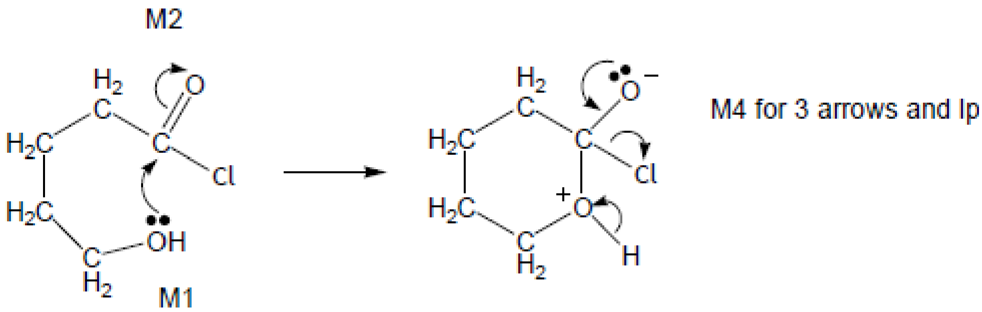
Q13.

(a) (i) (nucleophilic) <u>addition-elimination</u>

Not electrophilic addition-elimination

Ignore esterification

1



M3 for structure

- *If wrong nucleophile used or O–H broken in first step, can only score M2.*
- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2.*
- *If Cl lost with C=O breaking lose M2.*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4.*
- *Only allow M4 after correct / very close M3.*
- *Ignore HCl shown as a product.*

4

a 20-50 (ppm) or single value or range entirely within this range

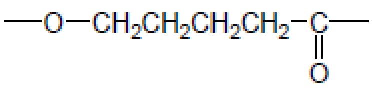
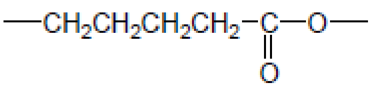
If values not specified as a or b then assume first is a.

1

b 50-90 (ppm) or single value or range entirely within this range

1

(ii)

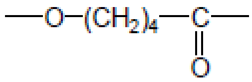
 **OR** 

Must have trailing bonds, but ignore n.

1

OR –$OCH_2CH_2CH_2CH_2CO$– **OR** –$CH_2CH_2CH_2CH_2COO$–

Allow



but not - C_4H_8-

one unit only

Condensation

1

(b)

	Tollens'	Fehling's / Benedicts	Acidified potassium dichromate

Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on.

1

J	No reaction / no (visible) change / no silver mirror	No reaction / no (visible) change / stays blue / no red ppt	No reaction / no (visible) change / stays orange / does not turn green

Ignore 'clear', 'nothing'.

Penalise wrong starting colour for dichromate.

1

K	Silver mirror / grey ppt	Red ppt (allow brick red or red-orange)	(orange) turns green

1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

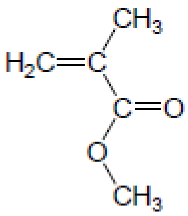
Ignore details of splitting.

If values not specified as J or K then assume first is J.

1

(c) If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.

L
ester



OR $H_2C{=}C(CH_3)COOCH_3$

All $C_5H_8O_2$ L to P must have C=C.

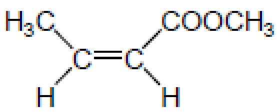
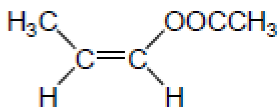
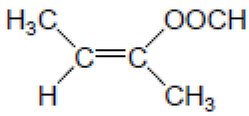
Allow CH_3–.

Allow -CO_2CH_3 etc.

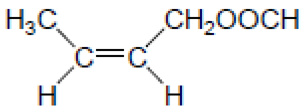
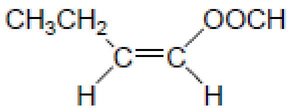
Allow $CH_2C(CH_3)COOCH_3$.

1

M
ester

 **OR**  **OR** 

$CH_3CH{=}CHCOOCH_3$ $CH_3CH{=}CHOOCCH_3$ $CH_3CH{=}C(CH_3)OOCH$

OR  **OR** 

$CH_3CH{=}CHCH_2OOCH$ $CH_3CH_2CH{=}CHOOCH$

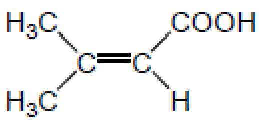
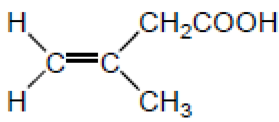
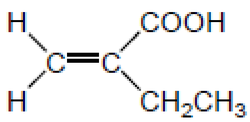
Allow either E–Z isomer.

Allow CH_3− or C_2H_5− but not CH_2CH_3−.

Allow $CH_3CHCHCOOCH_3$ etc.

1

N
acid

 **OR**  **OR** 

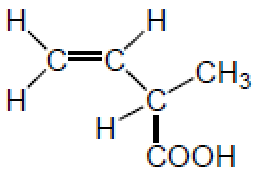
$(CH_3)_2C{=}CHCOOH$ $H_2C{=}C(CH_3)CH_2COOH$ $H_2C{=}C(COOH)CH_2CH_3$

Allow CH_3− or C_2H_5− but not CH_2CH_3−.

Allow −CO_2H.

Not cyclic isomers.

Not the optically active isomer.

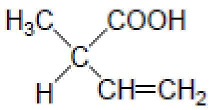


which is P anyway

Allow $(CH_3)_2CCHCOOH$ etc.

1

P
acid



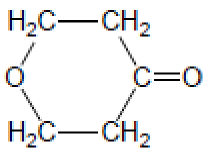
Allow $-CO_2H$.

$CH_3CH(COOH)CH{=}CH_2$

Allow $CH_3CH(CO_2H)CHCH_2$ or
$CH_3CH(CO_2H)C_2H_3$.

1

Q



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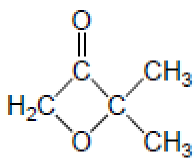

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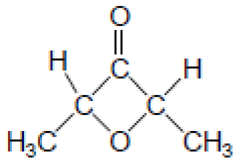


Not cyclic esters.

1

[19]

Q14.

(a) (i) <u>3</u>CH_3OH

Not molecular formula

1

$HOCH_2CH(OH)CH_2OH$

1

(ii) $\rightarrow$ $19CO_2$ + $19H_2O$

Or doubled

1

$C_{17}H_{35}COOCH_3$ + 27½ or 55/2 O_2

Consequential on correct right-hand side

1

(b) (i) A0.7

1

Ethanol6.4

1

Water3.6

1

(ii) No effect

If wrong, CE = 0

1

Equal moles on each side of equation ***OR*** V cancels

Ignore moles of gas

1

(iii) M1 $K_c = \frac{[\text{DEM}][H_2O]^2}{[A][C_2H_5OH]^2}$

Must have all brackets but allow ( )

1

(iv) M2 $\frac{2.1 \times (3.4)^2}{0.85 \times (7.2)^2}$

If K_c wrong can only score M4 for units consequential to their K_c working in (b)(iv)

1

M3 0.55 (min 2dp)

1

M4 No units

1

[13]

Q15.

(a) $Mg + 2C_6H_4(OH)COOH \rightarrow (C_6H_4(OH)COO)_2Mg + H_2$

Accept multiples, including fractions.

1

(b) Gas syringe / inverted burette over water / measuring cylinder over water

Collection apparatus must show graduations or be clearly labelled (eg syringe, burette, measuring cylinder).

1

[2]

Q16.

(a) $CH_3(CH_2)_{14}COOH$

Allow molecular formulae.

1

$CH_2OHCHOHCH_2OH$

Allow one mark only if formulae are swapped in position.

1

(b) Keeping the foodstuff dry

Allow an answer which refers to removal of water from the environment.

Do not allow dehydration / removal of water from the fat.

1

(c) They (antioxidants) react with free radicals

1

And they are used up in the reaction / do not remain behind after reaction

Lose one mark for any reference to 'catalysts can't slow down a reaction'.

1

(d) Mol of fat = (2.78 / 806 =) 3.45×10^{-3}

Mol of NaOH = 3.68×10^{-3} *= mol of fatty acid*

1

Mol of NaOH = 3.68×10^{-3}

Mol of fat hydrolysed = 1.23×10^{-3}

1

Mol of fat hydrolysed = (3.68×10^{-3} / 3 =) 1.23×10^{-3}

Mass of fat hydrolysed = 0.987 g

1

Percentage hydrolysed = 35.5 – 35.7

Percentage hydrolysed = 35.5 – 35.7

Do not penalise precision at any point.

Since there are a variety of approaches to this calculation, award four marks for a correct answer but it must be clear that there is some relevant working.

The answer alone gets M4 only.

Any incorrect use of the 3:1 ratio is CE – lose M3 and M4.

1

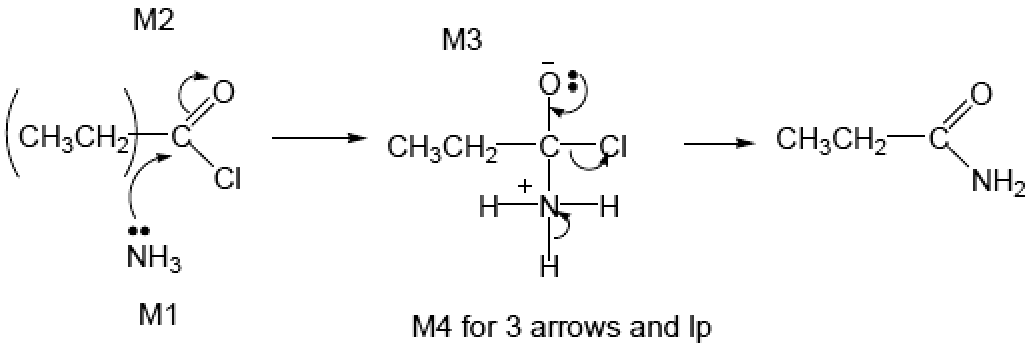
[9]

Q17.

(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 <u>with charges</u> 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

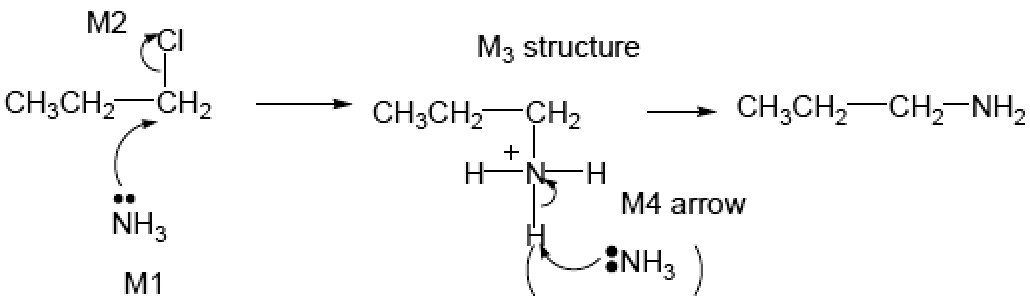
penalise propaneamide and N-propanamide

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-<u>1</u>-amine or <u>1</u>-aminopropane (<u>number 1 needed</u>)

penalise other numbers

allow <u>1</u>-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

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