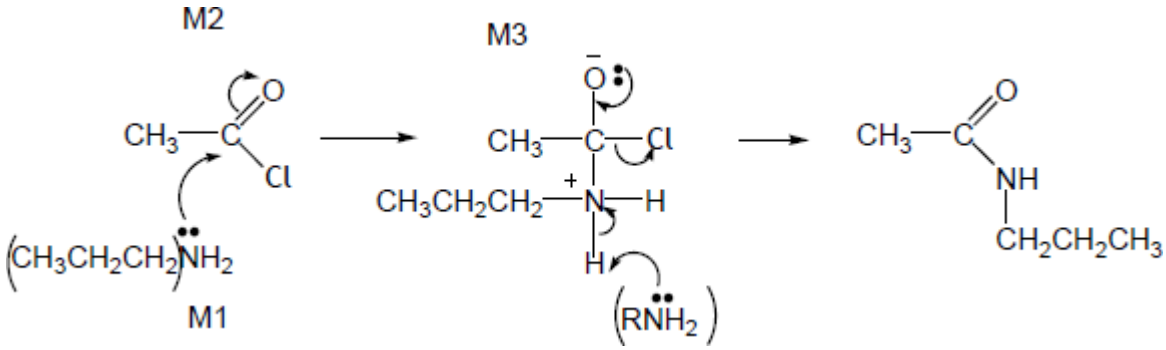
M1.(a) (nucleophilic) addition-elimination

1



M4 for 3 arrows and lp

Allow wrong amine in M1 but penalise in M3

Allow C_3H_7 in M3

Minus sign on NH_3 loses M1 (but not M4 if NH_3 also shown here)

- *Allow attack by: $NH_2CH_2CH_2CH_3$*
- *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, max 1 for M1*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4*
- *3 arrows in M4 can be shown in two separate steps.*
- *If M3 drawn twice, mark first answer eg ignore missing + if missed off second structure*
- *Only allow M4 after correct / very close M3*
- *For M4, ignore RNH_2 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism,*
- *but ignore HCl shown as a product.*

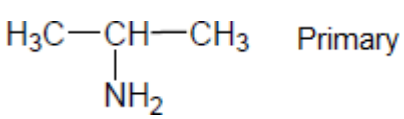
4

<u>N-propylethanamide</u> must be this name even if wrong amine used

NOT N-propylethaneamide

1

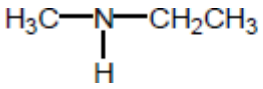
(b) (i)



Not allow ambiguous $C_3H_7NH_2$
BEWARE No mark for the original amine $CH_3CH_2CH_2NH_2$

Label and structure must both be correct for each type to score the mark.

1

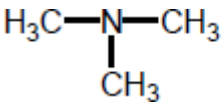


Secondary

Allow C_2H_5

Penalize wrong number of carbons but otherwise correct, first time only.

1



tertiary

1

(ii) Absorption at 3300−3500 (cm^{-1}) in spectrum

Allow trough, peak, spike.

Ignore absorption at 750 − 1100 for C–C bond in secondary - this is within fingerprint region.

Allow any number in this range.

If range missing, no further marks.

If range linked to tertiary, no further marks.

1

N–H (bond) (only) present in secondary amine or not present in tertiary amine
OR
This peak or N–H absorption (only) present in spectrum of secondary amine or not present in spectrum of tertiary amine

1

(c) (i) M1 Route **A**: stage 1 KCN

Apply list principle for extra reagents or catalysts
NOT HCN NOT KCN / acid Not KCN / HCN

1

M2 Aqueous or ethanolic

M2 only scores after correct M1

ignore warm; acid here loses M1 & M2

1

M3 Route **A** Intermediate CH_3CH_2CN or propanenitrile

If M3 intermediate wrong, max 2 for M1 & M2 ie no mark for stage 2

Name alone must be exactly correct to gain M1 but mark on if name close

But if M3 intermediate close, eg "nitrile" or wrong nitrile, can award marks in stage 2

correct formula gains M1 (ignore name if close)

If stage 1 correct and intermediate is missing, can award marks in stage 2

contradiction of name and formula loses mark

stage 1 wrong & intermediate missing, no marks.

1

M4 Route **A**: stage 2 H_2

H loses M4 but mark on

$LiAlH_4$

Apply list principle for extra reagents or catalysts.

M5 only scores after correct M4

Not $NaBH_4$ not Sn or Fe / HCl

Allow (dil) acid after but not with $LiAlH_4$

Penalise conc acid.

1

M5 Ni or Pt or Pd

ether

1

M6 Route **B** NH_3

With acid loses M6 & M7

Apply list principle for extra reagents or catalysts.

1

M7 Excess NH_3

Ignore conc, ignore high P, ignore solvent.

1

(ii) Route **A** disadv Toxic / poisonous KCN or cyanide or CN^- or HCN

Expensive $LiAlH_4$
ignore acidified

OR lower <u>yield</u> because 2 steps

Allow H_2 flammable / explosive etc.
Not just dangerous.
Ignore time reasons.

1

Route **B** disadv Further reaction / substitution likely

Allow impure product.

1

[20]

M2.(a) Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid
Allow H_2 (Ni / Pt) but penalise wrong metal
But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH

1

Equation must use molecular formulae

$C_6H_4N_2O_4 + 12\ [H]$

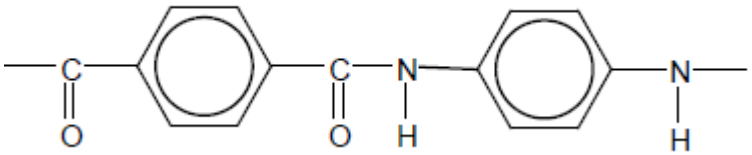
12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

1

$\rightarrow C_6H_8N_2 + 4H_2O$

Allow .... + $6H_2$ if H_2 / Ni used
Allow −CONH− or −COHN− or $-C_6H_4-$

1



Mark two halves separately: lose 1 each for

- *error in diamine part*
- *error in diacid part*
- *error in peptide link*
- *missing trailing bonds at one or both ends*
- *either or both of H or OH on ends*

Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal

NOT Sn / HCl, $NaBH_4$ etc.

1

CH_2

1

In benzene 120°

1

In cyclohexane 109° 28’ or 109½°

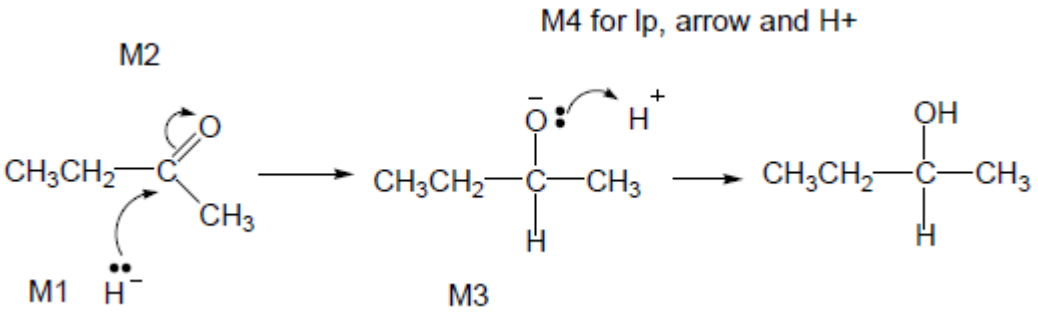
Allow 108° - 110°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

1



- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *M3 is for correct structure including minus sign but lone pair is part of M4*
- *Allow C_2H_5*
- *M1 and M4 include lp and curly arrow*
- *Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)*

4

(ii) M1 Planar C=O (bond / group)
Not just planar molecule

1

M2 Attack (equally likely) from either side
Not just planar bond without reference to carbonyl

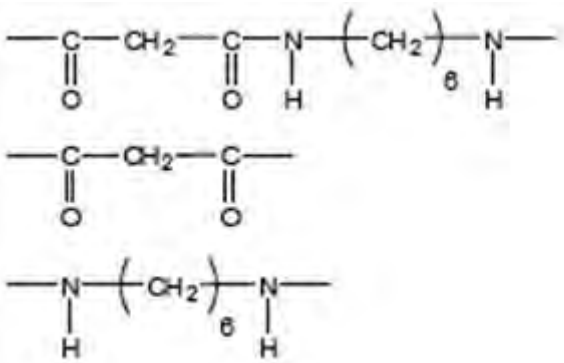
1

M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely

1

[17]

M3. (a) (i)



Allow –CONH- or - COHN -

Mark two halves separately

lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends

1

Not allow –(C_6H_{12})–

Ignore n

1

(ii) **M1** in polyamides - H bonding

1

M2 in polyalkenes - van der Waals forces

Penalise forces between atoms or van der Waals bonds

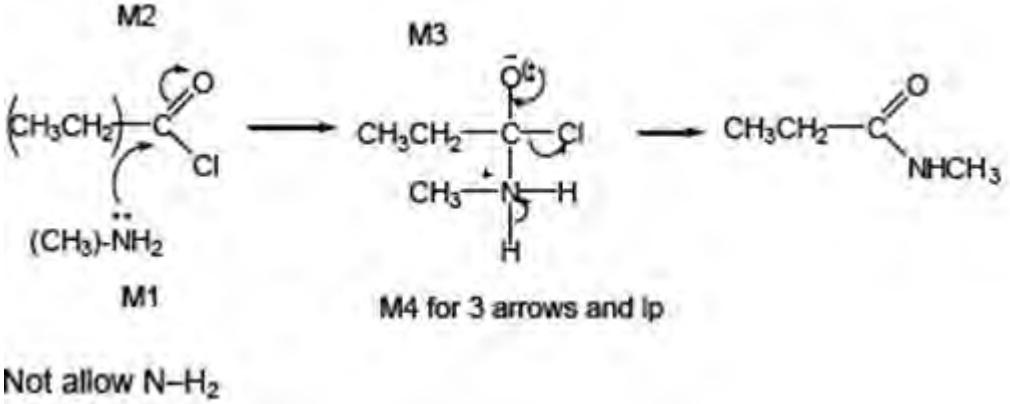
1

M3 Stronger forces (of attraction) in polyamides
Or H bonding is stronger
(must be a comparison of correct forces to score M3)

Do not award if refer to stronger bonds

1

(b) (i) (nucleophilic) addition elimination



Not allow N–H_2

*Minus sign on NH_2 loses **M1***

1

*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, max 1 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 as a product

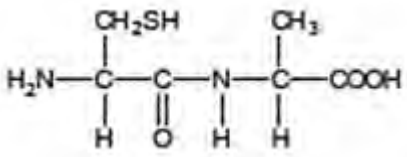
4

(ii) <u>N-methylpropanamide</u>

Not N-methylpropaneamide

1

(c)



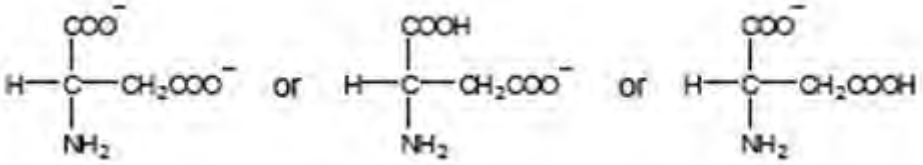
Allow –CONH– or –COHN–

1

(d) (i) <u>2-amino-3-hydroxypropanoic acid</u>

1

(ii)



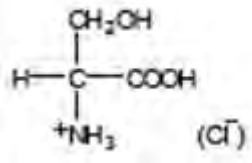
Must be salts of aspartic acid

allow $–CO_2^-$

allow $NH_2–$

1

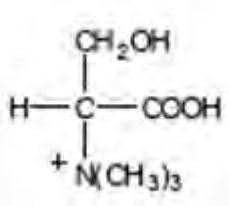
(iii) Penalise use of aspartic acid once in d(iii) and d(iv)



allow –CO_2H
allow $^+NH_3$–
don't penalize position of + on NH_3

1

(iv) Penalise use of aspartic acid once in d(iii) and d(iv)



(Br^-)

allow –CO_2^-
must show C-N bond
don't penalize position of + on $N(CH_3)_3$

1

[16]