M1.(a) M1 Lone pair on N labelled b more available / more able to be donated than lone pair on N labelled *a*

Ignore N(b) more readily accepts protons.

Ignore N(b) is stronger base.

1

M2 lp or electrons or electron density on N labelled *a:*

delocalized into (benzene) ring

QoL

1

M3 lp or electrons or electron density on N labelled *b:*

methyl / alkyl groups electron releasing or donating or (positive) inductive effect or push electrons or electron density

QoL

1

(b) $C_{19}H_{24}N_2$

Any order.

1

11

1

[5]

M2. (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

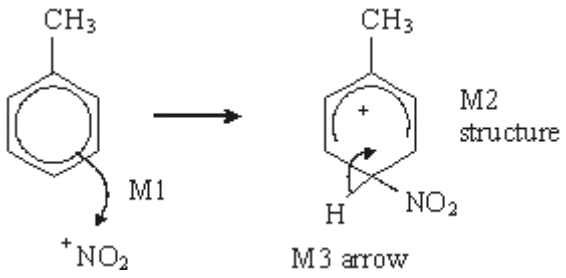
1

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$

1

(iii) electrophilic substitution CH_3



horseshoe must not extend beyond C2 to C6 but can be smaller
+ must not be too close to Cl

1

3

(b) Sn or Fe / HCl (conc or dil or neither)
or Ni / H_2 not $NaBH_4$ $LiAlH_4$

1

(c) (i) NH_3

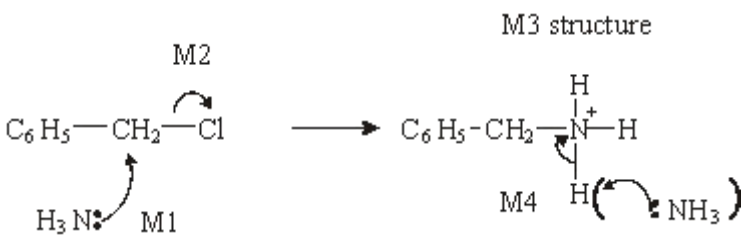
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

1



4

[15]

M3. D

[1]

M4. (a) **M1** Benzene is more stable than cyclohexatriene

more stable than cyclohexatriene must be stated or implied

If benzene more stable than cyclohexene, then penalise M1 but mark on

If benzene less stable: can score M2 only

1

M2 Expected $\Delta H^{\ominus}$ hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected $\Delta H^{\ominus}$ hydrog is three times the $\Delta H^{\ominus}$ hydrog of cyclohexene

1

M3 Actual $\Delta H^{\ominus}$ hydrogenation of benzene is

152 kJ mol^{-1} (less exothermic)

or 152 kJ mol^{-1} different from expected

Ignore energy needed

1

M4 Because of delocalisation or electrons spread out or resonance

1

(b) **No mark for name of mechanism**

Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation

1

$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$

OR

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

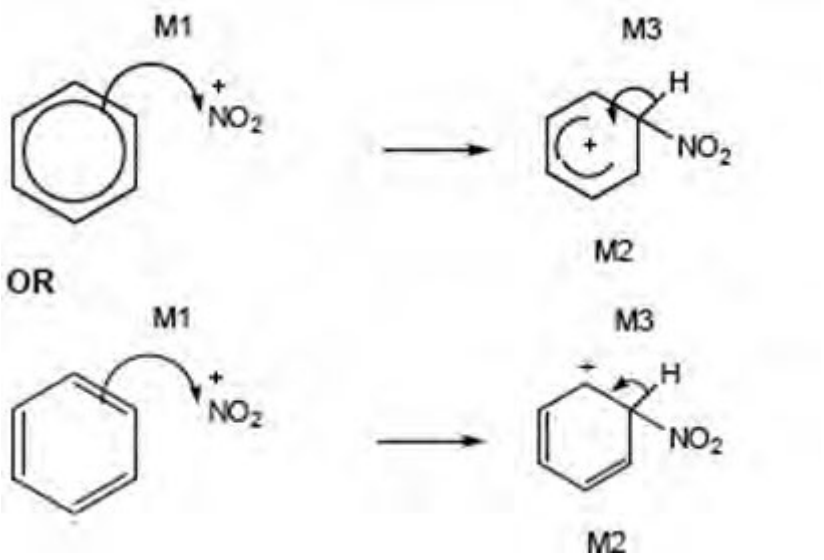
OR via two equations

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

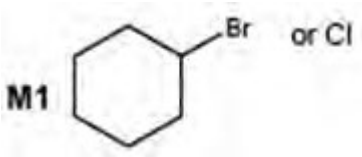
1



M1 arrow from within hexagon to N or + on N
Allow NO_2^+ in mechanism
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure
ignore base removing H in M3
+ on H in intermediate loses M2 not M3

3

(c) **If intermediate compound V is wrong or not shown, max 4 for 8(c)**



or chlorocyclohexane or bromocyclohexane

1

Reaction 3

M2 HBr

1

M3 Electrophilic addition

Allow M2 and M3 independent of each other

1

Reaction 4

M4 Ammonia if wrong do not gain M5

1

Allow M4 and M6 independent of each other

M5 Excess ammonia or sealed in a tube or under pressure

1

If CE e.g. acid conditions, lose M4 and M5

M6 Nucleophilic substitution

1

(d) Lone or electron pair on N

No marks if reference to ''lone pair on N'' missing

1

Delocalised or spread into ring in U

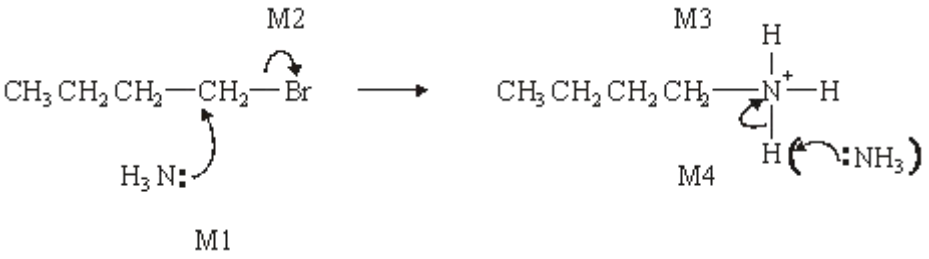
1

Less available (to accept protons) or less able to donate (to H^+)

1

[19]

M1. (a) Nucleophilic substitution



1

M1, M2 and M4 for arrows, M3 for structure of cation

(Allow M2 alone first, i.e. SN1 formation of carbocation)

(Penalise M4 if Br^- used to remove H^+)

4

(b) Step 1 $CH_3CH_2CH_2CN$ 1

$CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$ balanced

1

(or CN^-) (or Br^-)
(*not HCN*)

1

Step 2 $CH_3CH_2CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2CH_2NH_2$
(or 4[H])

1

(c) (i) Lone pair (on N) (in correct context)

1

R group increases electron density / donates electrons /pushes electrons / has positive inductive effect

1

(ii) Any strong acid (but not concentrated)
or any amine salt or ammonium salt of a strong acid

1

(d) $CH_3CH_2N(CH_3)_2$

1

[12]

M2. (a) Cyclohexane evolves 120 kJ mol^{-1}

$\therefore$ (expect triene to evole) 360 kJ mol^{-1} **(1)** or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

*QofL: benzene lower in energy / <u>more</u> (stated) stable **(1)***
Not award if mentions energy required for bond breaking

*due to <u>delocalisation</u> **(1)** or explained*

4

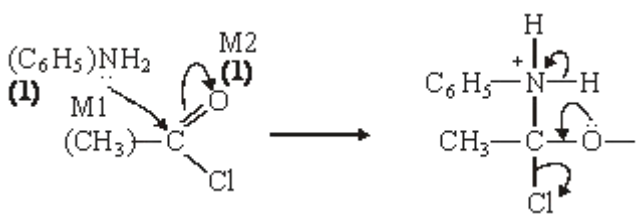
(b) (i) phenylamine weaker **(1)**

if wrong no marks

lone pair on N (less available) **(1)**
delocalised into ring **(1)** or "explained"

3

(ii) addition – elimination **(1)**



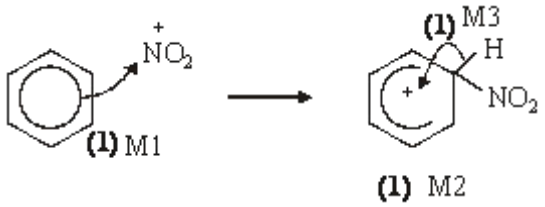
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)**
conc H_2SO_4 **(1)**

$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$ **(1)**



6

(iv) peptide / amide **(1)**

NaOH (aq) **(1)**

HCl conc or dil or neither

H_2SO_4 dil NOT conc

NOT just H_2O

2

Notes

(a)
- 360 or 3 × 120 or in words **(1)**;
- 152 NOT 150 **(1)**; (152 can get first two marks)
- **Q of L** benzene more stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene **(1)**;
- delocalisation or explained **(1)**

(b) (ii) or N-phenylacetamide or acetanilide

mechanism: if shown as substitution can only gain M1

if CH_3CO+ formed can only gain M1

lose M4 if Cl^- removes H^+

be lenient with structures for M1 and M2 but must be correct for M3

 alone loses M2

(iii) **No marks for name of mechanism in this part**

if conc missing can score one for both acids (or in equation)

allow two equations

allow $HNO_3 + H_2SO_4 \rightarrow NO^{2+} + HSO_4^- + H_2O$

ignore side chain in mechanism even if wrong

arrow for M1 must come from niside hexagon

arrow to NO_2^+ must go to N but be lenient over position of +

+ must not be too near "tetrahedral" Carbon

horseshoe from carbons 2-6 but don't be too harsh

(iv) reagent allow NaOH
HCl conc or dil or neither
H_2SO_4 dil or neither but not conc
not just H_2O

[21]

M3. B

[1]

M4. (a) (i) H+ or proton acceptor **(1)**
$CH_3NH_2 + H_2O$ (⇌) $CH_3^+NH_3$ (+) OH^- **(1)**

(ii) CH_3NH_3Cl or HCl **(1)**
Or any ammonium compound or strong acid name or formula

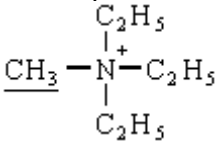
(iii) extra OH^- reacts with $CH_3\overset{+}{N}H_3$
or reaction / equilibrium moves to left
or ratio salt / base remains almost constant **(1)**
Any 2

5

(b) lone pair (on N accepts H^+) **(1)**
CH_3 increases electron density (on N)
donates / pushes electrons
has positive inductive effect **(1)**

2

(c) nucleophilic substitution **(1)**



(1)

2

[9]

M1.(a) Electrophilic substitution

Both words needed

Ignore minor misspellings

1

(b) (i) Sn / HCl

OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

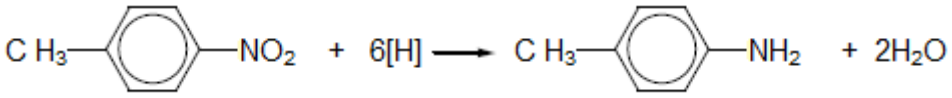
Ignore NaOH after Sn / HCl

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

OR



Allow molecular formulae as structures given

$C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

OR making hair conditioner

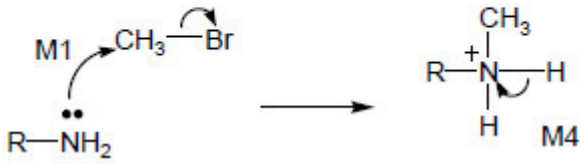
OR making fabric softener

OR making detergents

1

(c)

M2



M3

NO Mark for name of mechanism

Allow SN1

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

M2 for arrow from bond to Br

M3 for structure of protonated secondary amine

M4 for arrow from bond to N or + on N

For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br^-

4

(d) <u>lone or electron pair on N</u>

If no mention of lone pair CE = 0

If lone pair mentioned but not on N then lose M1 and mark on

M1

1

in **J** spread / delocalised into ring (or not delocalised in K)

Ignore negative inductive effect of benzene

*Allow interacts with **Π** cloud for M2*

M2

1

less available (for protonation or donation in **J**)

M3

OR

in **K** there is a positive inductive effect / electron releasing)

M2

more available (for protonation or donation in **K**)

M3

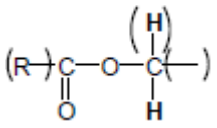
1

[11]

M2.(a) M1 Ester **1**

If Ester 2, can score M3 only.

1

M2 peak at δ = 4.1 due to 

When marking M2 and M3, check any annotation of structures in the stem at the top of the page.

1

M3 (δ = 4.1 peak is) quartet as <u>adjacent / next to / attached to CH_3</u>

1

M4 Other spectrum quartet at δ = 2.1-2.6 (or value in this range)

1

(b) M1 <u>Quaternary</u> (alkyl) <u>ammonium salt / bromide</u>

1

M2 CH_3Br or bromomethane

Penalise contradictory formula and name.

1

M3 Excess (CH_3Br or bromomethane)

Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3.

1

M4 Nucleophilic substitution

Can only score M3 if reagent correct.

Ignore alcohol or ethanol (conditions) or Temp.

1

(c)

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.

If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change

Ignore 'clear', 'nothing'.

Allow colour fades slowly.

Allow 'nvc' for no visible change.

1

cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[11]

M3. (a) (i) $CH_3CH=CHCH_3$

1

Addition or radical (**QoL**)

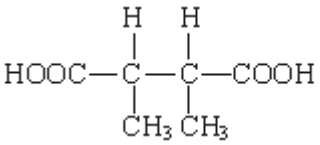
1

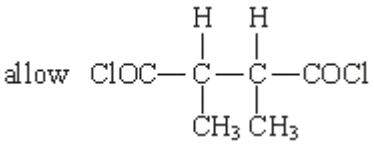
(ii) $CH_3CH(OH)CH(OH)CH_3$ or with no brackets

1

butan(e)–2,3–diol or 2,3–butan(e)diol

1



allow 

1

2,3–dimethylbutan(e)dioic acid 2,3–dimethylbutan(e)dioyl chloride

ignore –1,4–

1

condensation (**QoL**)

1

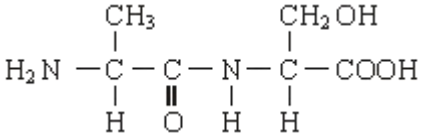
(iii) NaOH or HCl etc or Na_2CO_3

Allow conc sulphuric/nitric

***NOT** water nor acidified water nor weak acids*

1

(b) Structure 1



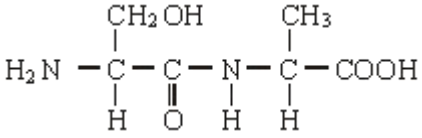
Allow –CONH– and –COHN–

Allow zwitterions

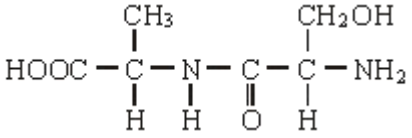
NOT polypeptides/repeating units

1

Structure 2 either of



or



1

(c) (i) $CH_3CH_2CH_2Br$

allow –Cl, –I

1

(ii) CH_3CH_2CN

1

(iii) (nucleophilic) substitution or from $CH_3CH_2CH_2Br$

if reduction written here, no further marks

1

further substitution/reaction occurs or other products are formed

Allow reduction forms only one product

1

one of
$(CH_3CH_2CH_2)_2NH$
$(CH_3CH_2CH_2)_3N$
$(CH_3CH_2CH_2)_4N^+ Br^-$

Allow salts including NH_4Br

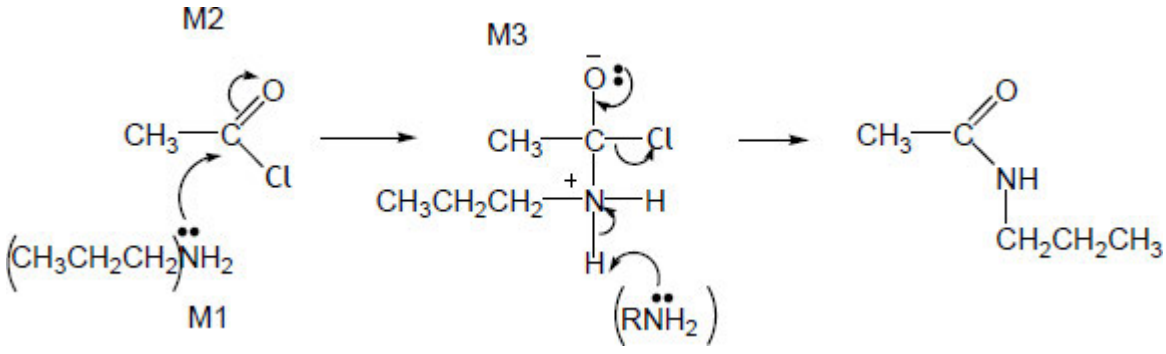
Allow HBr

1

[15]

M4.(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.*

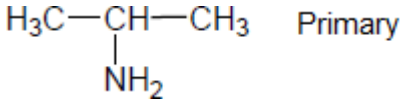
4

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

NOT N-propylethaneamide

1

(b) (i)



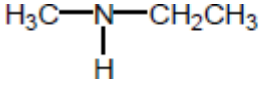
Primary

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

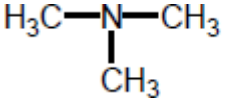


Secondary

Allow C_2H_5

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

1



tertiary

1

(ii) Absorption at <u>3300−3500</u> (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

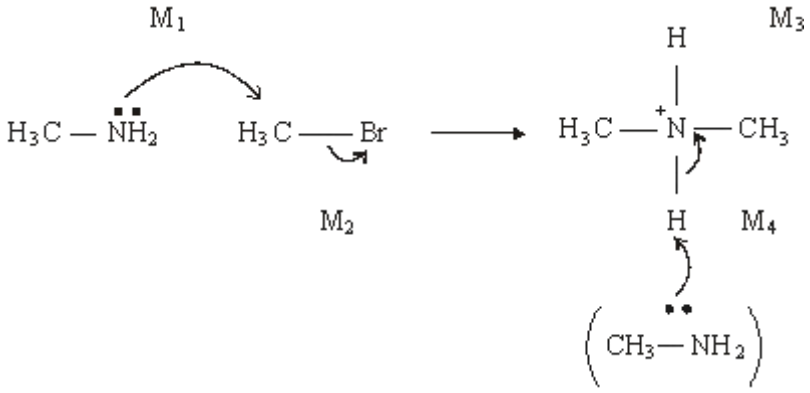
[20]

M1. (a) dimethylamine

1

(b) nucleophilic substitution

1



4

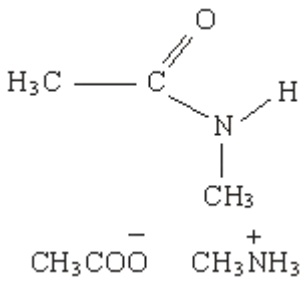
(c) quaternary ammonium salt

1

(cationic) surfactant / bactericide / detergent / fabric softener or conditioner/hair conditioner

1

(d)



(allow CH_3COOH or CH_3COO^- NH_4^+)

2

[10]

M2. **X** is CH_3CN or ethanenitrile or ethanonitrile or methyl cyanide or cyanomethane or ethyl nitrile or methanecarbonitrile

***Not** ethanitrile*
but contradiciton of name and structure lose marks

1

Y is $CH_3CH_2NH_2$ or ethylamine or aminoethane or ethanamine

1

Step 1: reagent KCN not HCN/HCl
condition (aq)/alcohol - only allow condition if reagent correct or incomplete

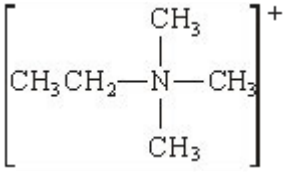
2

Step 2: reagent H_2 $LiAlH_4$ Na Zn/Fe/Sn Not $NaBH_4$
condition Ni/Pt/Pd ether ethanol HCl

2

Z is an amine or aminoalkane or named amine even if incorrect name for **Z** secondary (only award if amine correct)

1



(Br^-) + can be on N or outside brackets as shown

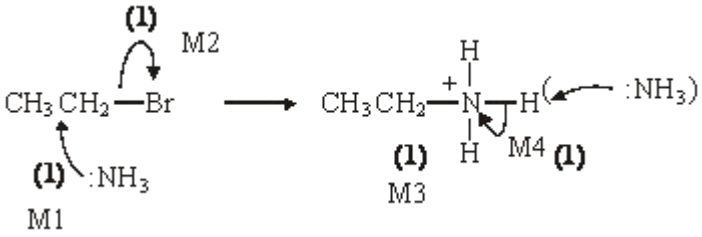
1

nucleophilic substitution

1

[9]

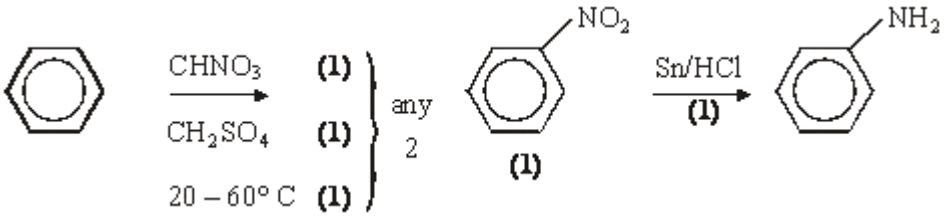
M3. (a)



Further reaction / substitution / formation of 2° / 3° amines etc **(1)**
use an excess of NH_3 **(1)**

6

(b)  repels nucleophiles (such as NH_3) **(1)**



5

Notes

(a) allow S_N1
penalise: Br^- intead of NH_3 removing H^+ for M4
not contamination with *other amines* (this is in the question) not diamines

(b) allow because NH_3 is a nuclephile or benzene is (only) attacked by electrophiles
or C–Br bond (in bromobenzene) is stronger / less polar or Br lp delocalized

HNO_3 / H_2SO_4 without either conc scores **(1)** allow 20 – 60° for **(1)** (any 2 ex 3)

allow name or structure of nitrobenzene

other reducing agents: Fe or Sn with HCl (conc or dil or neither)
not conc H_2SO_4 or conc HNO_3
allow Ni/H_2
Not $NaBH_4$ or $LiAlH_4$
ignore wrong descriptions for reduction step e.g. hydrolysis or hydration

[11]

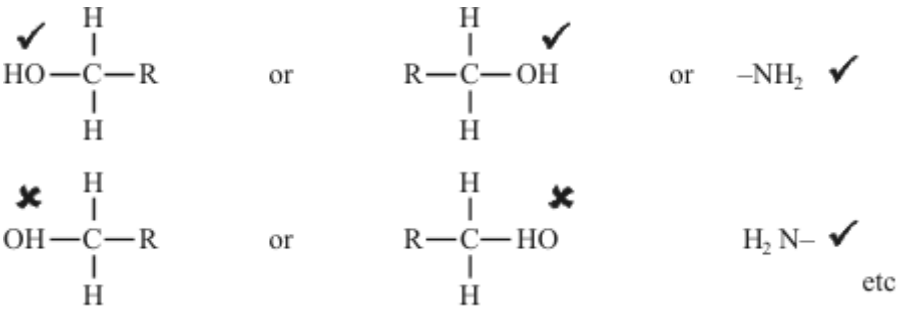
Organic points

(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH_3– or $–CH_3$ or  or CH_3
or H_3C–

M4. (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

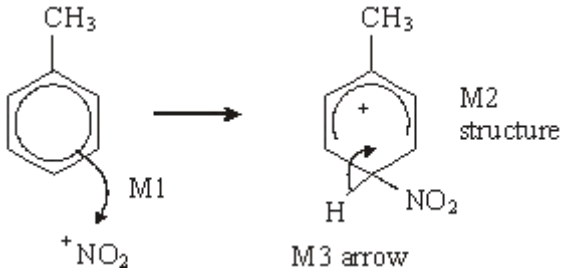
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$

1

(iii) electrophilic substitution CH_3

1



horseshoe must not extend beyond C2 to C6 but can be smaller
+ must not be too close to Cl

3

(b) Sn or Fe / HCl (conc or dil or neither)
or Ni / H_2 not $NaBH_4$ $LiAlH_4$

1

(c) (i) NH_3

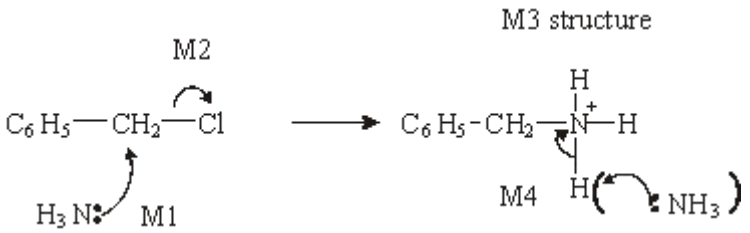
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

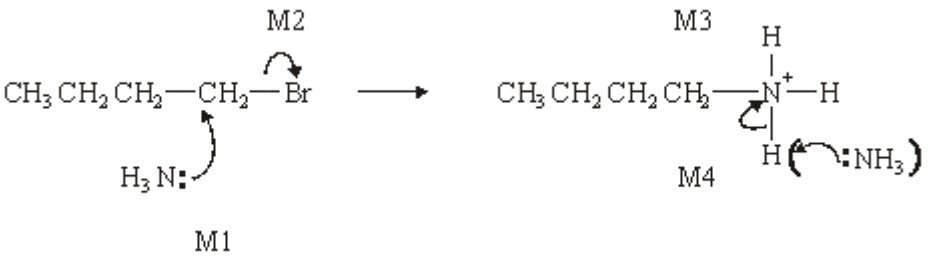
1



4

[15]

M5. (a) Nucleophilic substitution



1

M1, M2 and M4 for arrows, M3 for structure of cation
(Allow M2 alone first, i.e. SN1 formation of carbocation)

(Penalise M4 if Br^- used to remove H^+)

4

(b) Step 1 $CH_3CH_2CH_2CN$ 1

$CH_3CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CN + KBr$ balanced

1

(or CN^-) (or Br^-)
(*not HCN*)

1

Step 2 $CH_3CH_2CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2CH_2NH_2$
(or 4[H])

1

(c) (i) Lone pair (on N) (in correct context)

1

R group increases electron density / donates electrons /pushes electrons / has positive inductive effect

1

(ii) Any strong acid (but not concentrated)
or any amine salt or ammonium salt of a strong acid

1

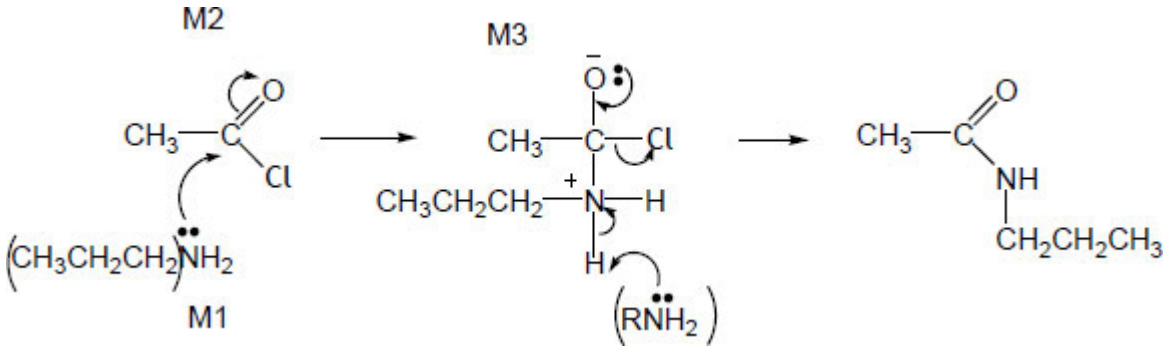
(d) $CH_3CH_2N(CH_3)_2$

1

[12]

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.*

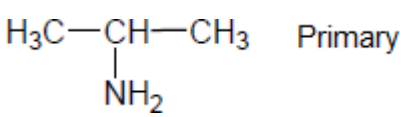
4

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

NOT N-propylethaneamide

1

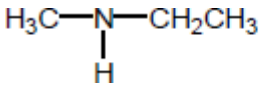
(b) (i)



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

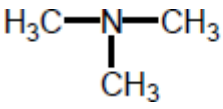


Secondary

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

$C_6H_4N_2O_4 + 12\,[H]$

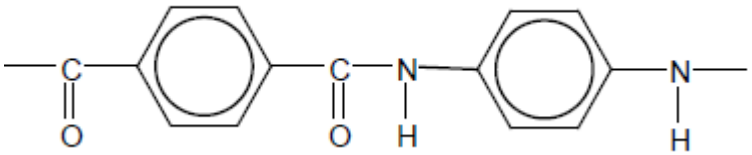
12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

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°

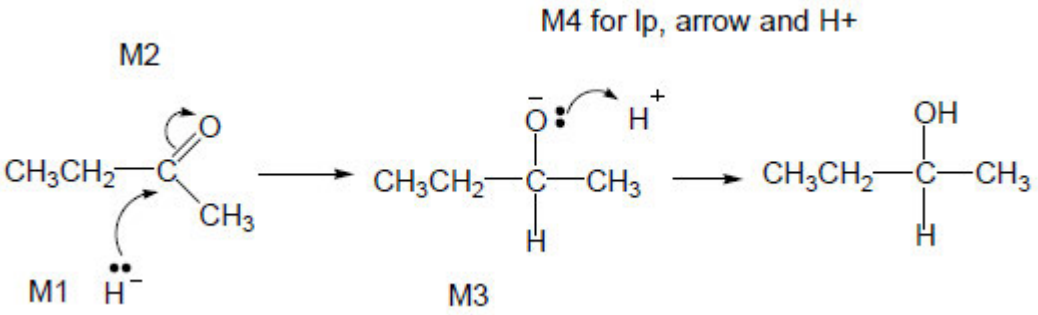
Allow 108° - 110°

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

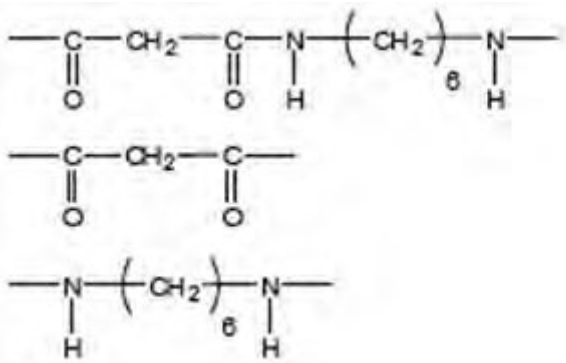
1

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

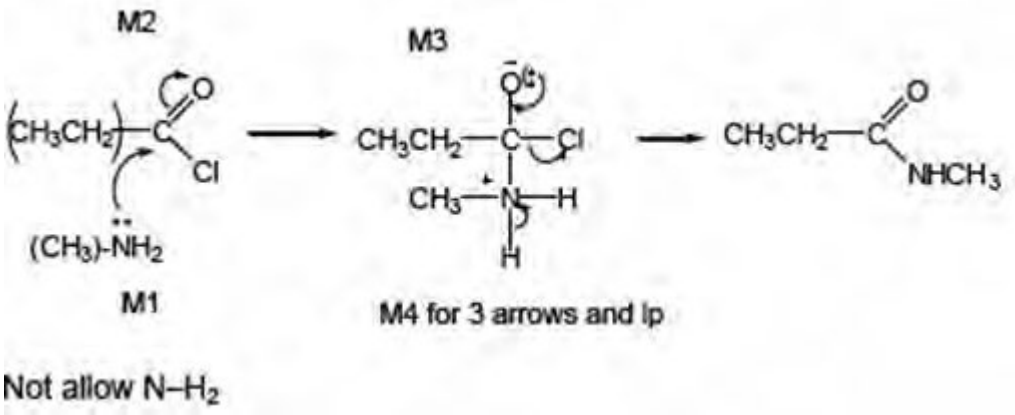
1

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

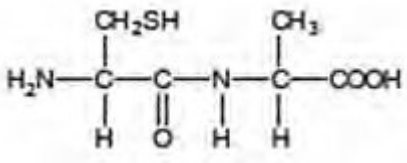
4

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

Not N-methylpropaneamide

1

(c)



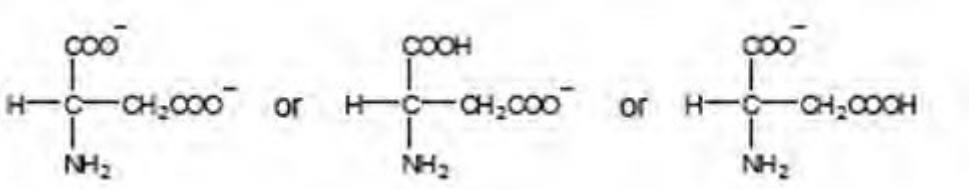
Allow –CONH– or –COHN–

1

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

1

(ii)



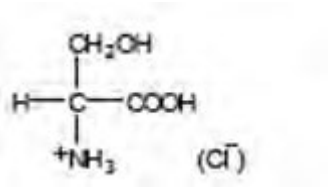
Must be salts of aspartic acid

allow $–CO_2^-$

allow $NH_2–$

1

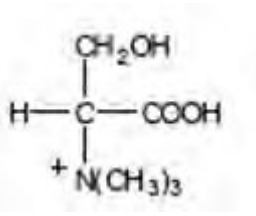
(iii) Penalise use of aspartic acid once in d(iii) and d(iv)



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]

M1. (a) **M1** Benzene is more stable than cyclohexatriene

more stable than cyclohexatriene must be stated or implied

If benzene more stable than cyclohexene, then penalise M1 but mark on

If benzene less stable: can score M2 only

1

M2 Expected $\Delta H^{\ominus}$ hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected $\Delta H^{\ominus}$ hydrog is three times the $\Delta H^{\ominus}$ hydrog of cyclohexene

1

M3 Actual $\Delta H^{\ominus}$ hydrogenation of benzene is

152 kJ mol^{-1} (less exothermic)

or 152 kJ mol^{-1} different from expected

Ignore energy needed

1

M4 Because of delocalisation or electrons spread out or resonance

1

(b) **No mark for name of mechanism**

Conc HNO_3

If either or both conc missing, allow one;

1

Conc H_2SO_4

this one mark can be gained in equation

1

$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$

OR

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$

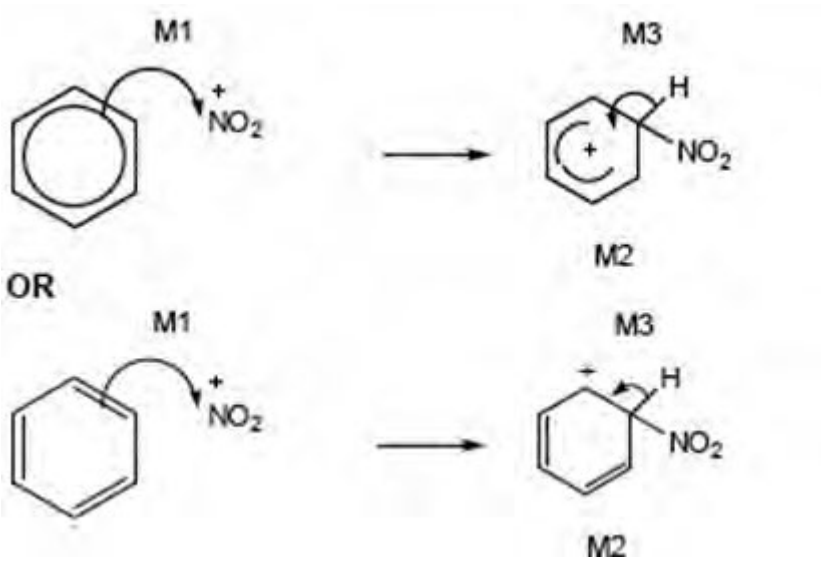
OR via two equations

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



M1 arrow from within hexagon to N or + on N

Allow NO_2^+ in mechanism

horseshoe must not extend beyond C2 to C6 but can be smaller

+ not too close to C1

M3 arrow into hexagon unless Kekule

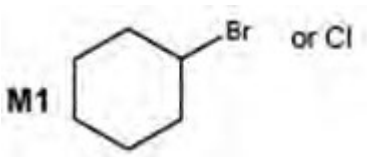
allow M3 arrow independent of M2 structure

ignore base removing H in M3

+ on H in intermediate loses M2 not M3

3

(c) **If intermediate compound V is wrong or not shown, max 4 for 8(c)**



or chlorocyclohexane or bromocyclohexane

1

Reaction 3

M2 HBr

1

M3 Electrophilic addition

Allow M2 and M3 independent of each other

1

Reaction 4

M4 Ammonia if wrong do not gain M5

1

Allow M4 and M6 independent of each other

M5 Excess ammonia or sealed in a tube or under pressure

1

If CE e.g. acid conditions, lose M4 and M5

M6 Nucleophilic substitution

1

(d) Lone or electron <u>pair on N</u>

No marks if reference to ''lone pair on N'' missing

1

Delocalised or spread into ring in U

1

Less available (to accept protons) or less able to donate (to H^+)

1

[19]

M2. (a) (i) **W** 3

1

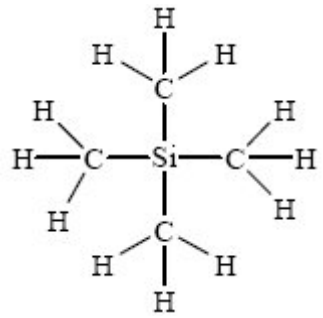
X 4

1

Y 2

1

(ii)



displayed formula shows ALL bonds

1

(b) (i) NO_2^+

allow + anywhere
can score in equation

1

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

1

OR

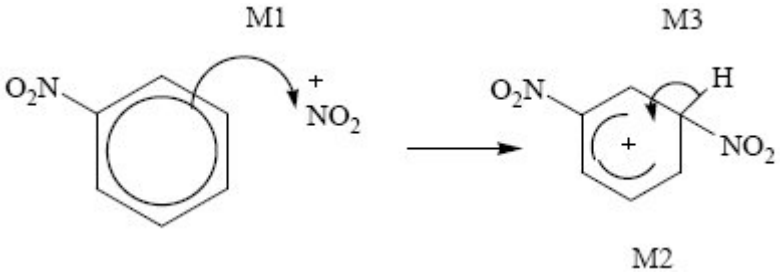
$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

or use two equations via $H_2NO_3^+$

(ii) electrophilic substitution

Not Friedel Crafts

1



Allow Kekule structures
+ must be on N of $^+NO_2$ (which must be correct)
both NO_2 must be correctly positioned and bonded to gain M2

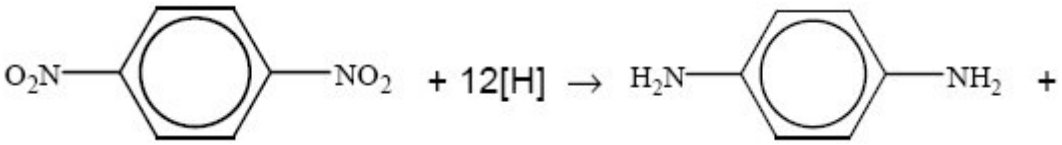
M1 arrow from circle or within it to N or to + on N
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure
ignore base removing H in M3

3

(c) (i) H_2/Ni or H_2/Pt or Sn/HCl or Fe/HCl (conc or dil or neither)
allow dil H_2SO_4
ignore mention of NaOH

Not $NaBH_4$
Not $LiAlH_4$
Not Na/C_2H_5OH
not conc H_2SO_4 or any HNO_3

1

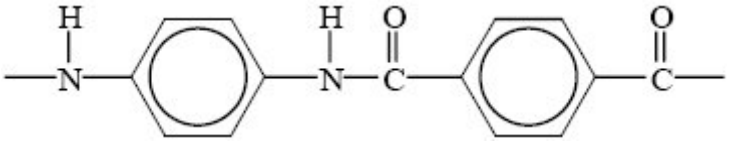


$4H_2O$
Or $6H_2$

allow $C_6H_4(NO_2)_2$ etc ,
allow NO_2– NH_2–
i.e. be lenient on structures, the mark is for balancing equ

1

(ii)



allow –CONH
ignore [ ]$_n$ as in polymer

1st mark for correct peptide link
2nd mark for the rest correct including trailing bonds

2

(iii) **M1** Kevlar is <u>biodegradeable</u> but polyalkenes not
allow Kevlar is <u>more</u> biodegradeable

1

M2 Kevlar has <u>polar</u> bonds/is a (poly) amide/has peptide link
comment on structure of Kevlar

1

M3 can be hydrolysed/attacked by nucleophiles/acids/ bases/enzymes

1

M4 polyalkenes <u>non polar</u>/has <u>non-polar</u> bonds
comment on structure of polyalkenes but not just strong bonds

1

[18]

M3. **H** CH_3CN or ethanenitrile

1

S $CH_3CH_2NH_2$ or ethylamine 1Step 1 KCN

1

aq/alcoholic

1

Step 2 H_2

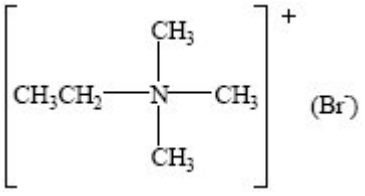
1

Ni

1

W secondary amine

1



1

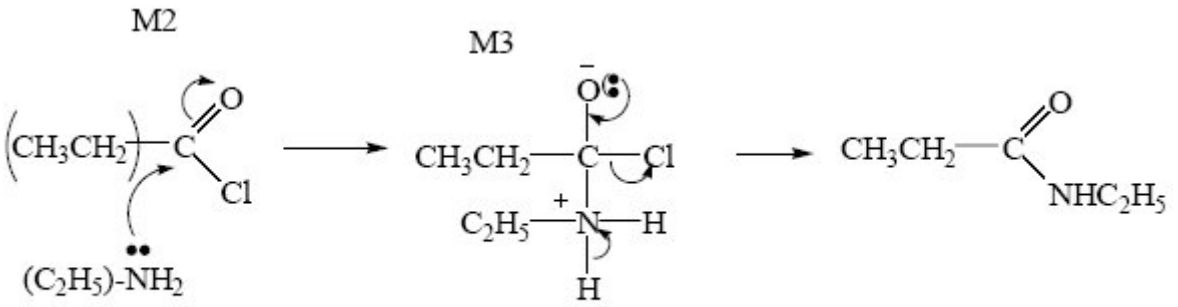
nucleophilic substitution

1

[9]

M4. (a) (nucleophilic) addition-elimination

1



4

N-ethylpropanamide

minus on NH_2 loses M1
M2 not allowed independent of M1, but allow M1 for correct attack on C+
+C=O loses M2
only allow M4 after correct or very close M3
lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
Not N-ethylpropaneamide

1

(b) CH_3CN or ethan(e)nitrile or ethanonitrile

not ethanitrile
but allow correct formula with ethanitrile

1

for each step wrong or no reagent loses condition mark

contradiction loses mark

1

Step 1 Cl_2
uv or above 300 °C

wrong or no reagent loses condition mark

1

Step 2 KCN

1

aq and alcoholic (both needed)

allow uv light/(sun)light/uv radiation

1

Step 3 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH

not CN^- but mark on
NOT HCN or KCN + acid, and this loses condition mark
NOT $NaBH_4$
Sn/HCl (forms aldehyde!)
ignore conditions

1

[12]