1

(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 ΔHº hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected ΔHº hydrog is three times the ΔHº hydrog of cyclohexene

1

M3 Actual ΔHº 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

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

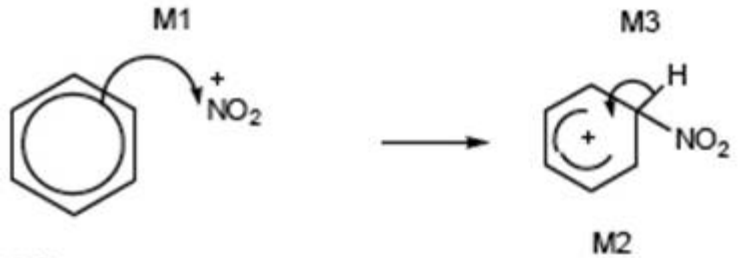
OR via two equations

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

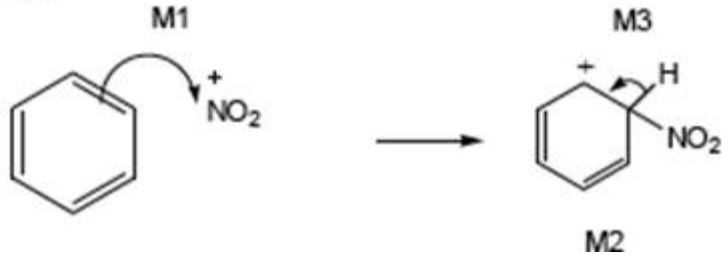
$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



OR



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

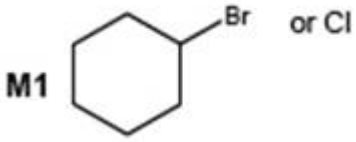
allow M3 arrow independent of M2 structure

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]

2

(a) **J** (acid) amide

not peptide, not N-substituted amide

1

K (secondary) amine or amino

penalise primary or tertiary
allow N-substituted amine

1

(b) (δ =) 3.1-3.9

1

doublet **OR** duplet

Not 3.7 – 4.1

Not secondary

name required not the number 2

1

(c) (i) Solvent must be proton-free

OR $CHCl_3$ has protons or has H or gives a peak

1

(ii) $CDCl_3$ is polar **OR** CCl_4 is non-polar

1

(d) 11 **OR** eleven

1

(e) (i) $Si(CH_3)_4$ **OR** SiC_4H_{12}

ignore TMS

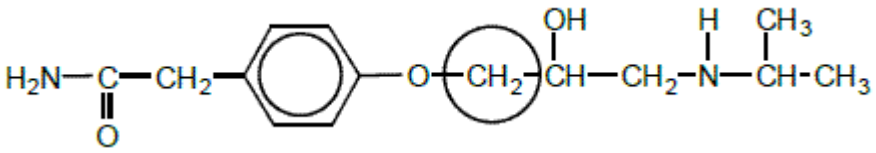
1

(ii) a single number or a range within 21-25

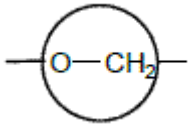
penalise anything outside this range

1

(iii)



allow ring around the C only and also allow



1

(f) (i) $NaBH_4$

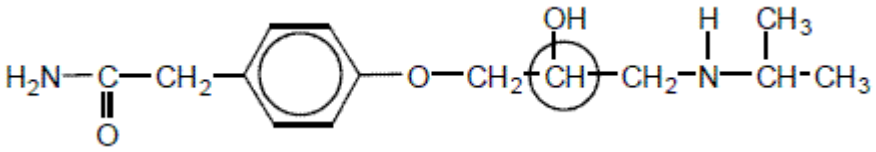
ignore name if formula correct

ignore solvent

allow $LiAlH_4$ Zn/HCl Sn/HCl H_2/Ni H_2/Pt

1

(ii)



allow ring around the C only

1

(iii) (plane) polarised light **OR** light in a polarimeter

1

polarised light is not rotated or is unaffected

penalise bent/diffracted/deflected/reflected

Not just solution is optically inactive

1

(iv) **adv** cheaper medicine due to cost or difficulty <u>of separation</u> or both can lower blood pressure

OR more effective/beneficial <u>with a reason</u>

or no need to separate

1

disadv may be side effects from one enantiomer in the mixture or only half the product works or one enantiomer may be ineffective or double dose required

1

[16]

3

(a) diethylamine **OR** ethyl ethanamine **OR** ethyl aminoethane

ignore N–

1

(b) For (b) and (c)

There are three valid routes for this synthesis called Routes **A**, **B** and **C** below

- Decide which route fits the answer best (this may not be the best for part b) to give the candidate the best possible overall mark.
- Mark part (b)
- For this best route mark the mechanism and reagent independently
- Migration from one route to another is not allowed
- Either name or formula is allowed in every case.
- Ignore conditions unless they are incorrect.

	Route A	Route B	Route C	
F	CH_3CH_2Br or CH_3CH_2Cl	C_2H_6	CH_3CH_2OH	1
G	$CH_3CH_2NH_2$ ethylamine OR ethanamine OR aminoethane	CH_3CH_2Br OR CH_3CH_2Cl	CH_3CH_2Br OR CH_3CH_2Cl	1

(c)

		Route A	Route B	Route C	
Step 1	Reagent(s)	HBr **OR** HCl	$\underline{H_2/Ni}$ (Not $NaBH_4$)	H_2O & H_3PO_4 **OR** H_2O & H_2SO_4	**1**
	Mechanism	Electrophilic addition	addition (allow electrophilic **OR** catalytic but not nucleophilic) ignore hydrogenation	Electrophilic addition	**1**
Step 2	Reagent(s)	NH_3	Cl_2 **OR** Br_2	HBr OR KBr & H_2SO_4 **OR** PCl_3 **OR** PCl_5 **OR** $SOCl_2$	**1**
	Mechanism	Nucleophilic substitution	(free) radical substitution	Nucleophilic substitution	**1**
Step 3	Reagent(s)	CH_3CH_2Br **OR** CH_3CH_2Cl	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	**1**
	Mechanism	Nucleophilic substitution	Nucleophilic substitution	Nucleophilic substitution	**1**

(d) tertiary amine **OR** triethylamine **OR** $(CH_3CH_2)_3N$
Quaternary ammonium salt
OR tetraethylammonium bromide **OR** chloride **OR** ion
OR $(CH_3CH_2)_4N^+$ (Br^- **OR** Cl^-)

1

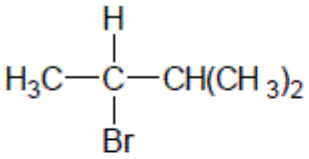
further substitution will take place **OR**
diethylamine is a better nucleophile than ethylamine

1

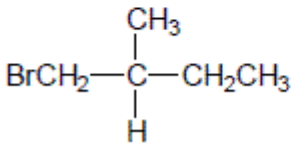
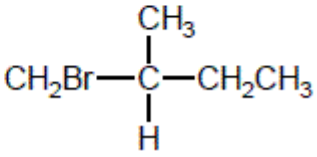
[11]

4

(a) (i)



must be **branched** and chiral

or  or 

not allow C_3H_7

allow C_2H_5 bonded to C either way round

1

(ii) elimination

allow base – elimination

but penalise any other qualification

1

(iii) Z-pent-2-ene or cis-pent-2-ene either Z or cis is necessary
(allow Z-2-pentene or cis-2-pentene)

with or without brackets around Z
with or without hyphens

1

(b) (i) C

1

(ii) A

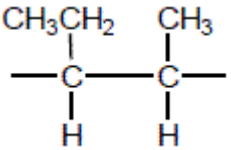
1

(iii) B

1

(iv) D

1

(c) 

allow C_2H_5 bonded via C or H

must have both trailing bonds
ignore brackets or n

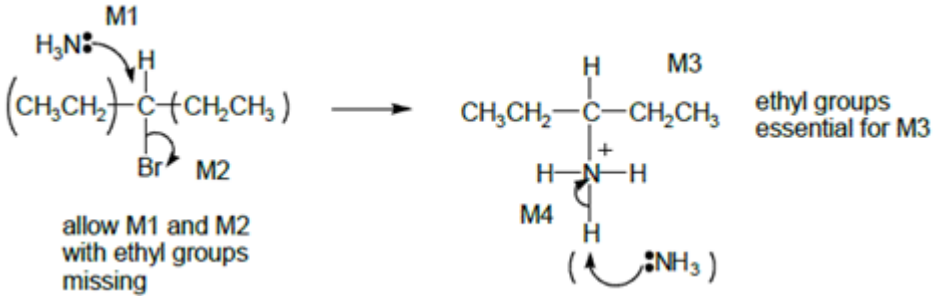
1

addition or radical or step or chain growth

QOL not additional

1

(d) (i)



Allow SN1, i.e M2 first then attack of NH_3 on carbocation.

Allow C_2H_5 in M3 bonded either way

Allow with or without NH_3 to remove H^+ in M4, but lose mark if Br^- used.

ignore δ+ or δ– unless wrong

+ on central C instead of δ + loses M2

4

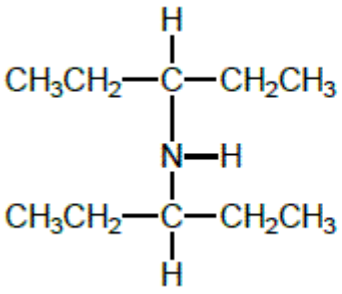
(ii) <u>excess</u> NH_3

ignore reflux

allow conc ammonia in sealed tube

1

(iii)

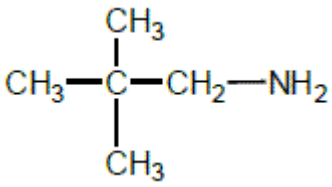


NOT $-C_5H_{11}$

Allow C_2H_5 bonded either way

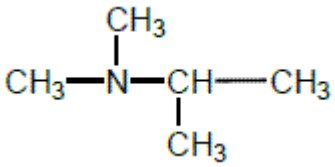
1

(e) (i)



1

(ii)



NOT $(C_2H_5)_2NCH_3$ which is tertiary with 3 peaks but its spectrum has no doublet.

1

[17]

5 (a) (i) **W** 3

1

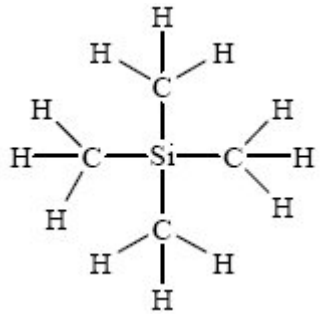
X 4

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

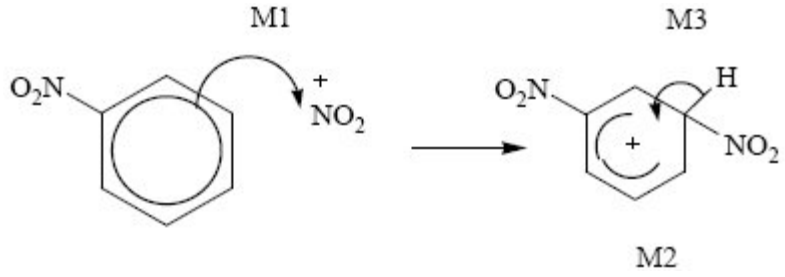
$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

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

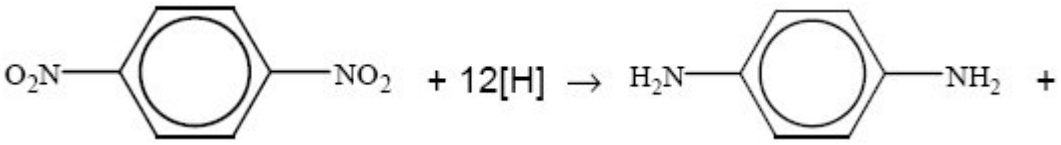
(c) (i) H_2/Ni or H_2/Pt or Sn/HCl or Fe/HCl (conc or dil or neither)

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

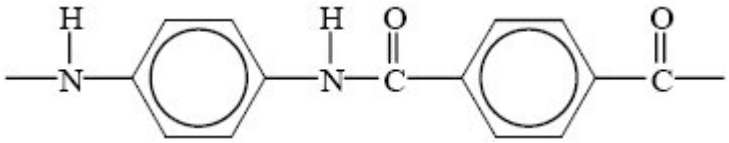


$4H_2O$

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

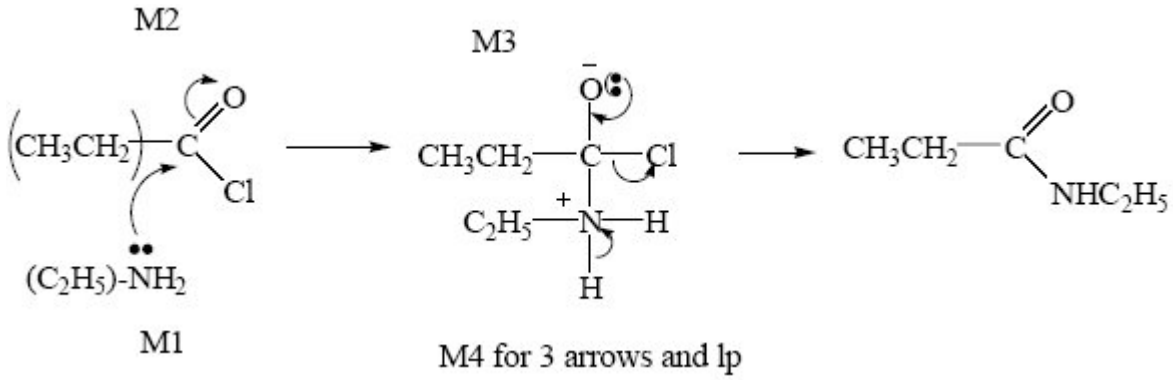
comment on structure of polyalkenes but not just strong bonds

1

[18]

6 (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]

7

H CH_3CN or ethanenitrile **1**

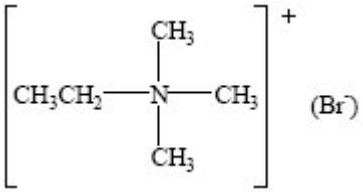
S $CH_3CH_2NH_2$ or ethylamine 1Step 1 KCN **1**

aq/alcoholic **1**

Step 2 H_2 **1**

Ni **1**

W secondary amine **1**



1

nucleophilic substitution **1**

[9]

8 Acidified potassium dichromate(VI)

Turns green with propan-2-ol and propanal **1**

No reaction with hexene and 1-bromopropane **1**

Tollens with propan-2-ol and propanal **1**

only propanal gives silver mirror **1**

Bromine water **1**

Decolourised by hexane **1**

No reaction with 1-bromopropane **1**

Warm NaOH followed by acidified $AgNO_3$ **1**

White ppt with 1-bromopropane **1**

[10]