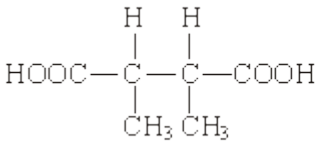
Mark schemes

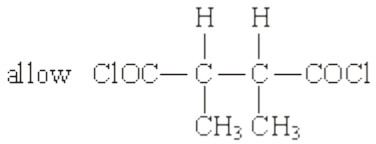
1 (a) (i) $CH_3CH=CHCH_3$ **1**

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**





1

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

ignore –1,4–

1

condensation (**QoL**) **1**

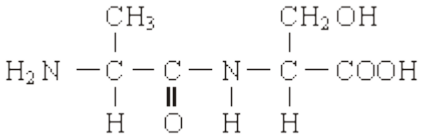
(iii) NaOH or HCl etc or Na_2CO_3

Allow conc sulphuric/nitric

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

1

(b) Structure 1



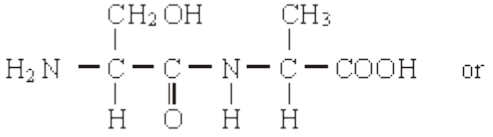
Allow –CONH– and –COHN–

Allow zwitterions

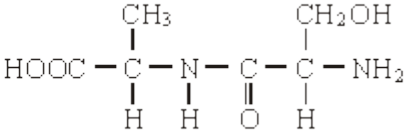
NOT polypeptides/repeating units

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

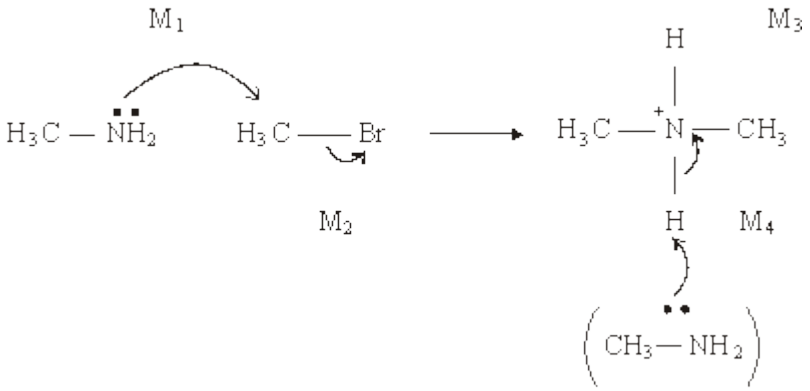
[15]

2 (a) dimethylamine

1

(b) nucleophilic substitution

1



4

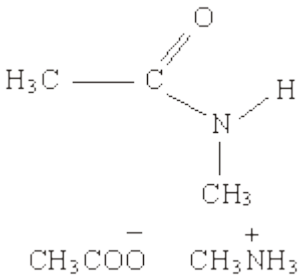
(c) quaternary ammonium salt

1

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

1

(d)



(allow CH_3COOH or $CH_3COO^-\ NH_4^+$)

2

[10]

3 D

[1]

4 (a) (i) conc HNO_3

1

conc H_2SO_4

allow 1 for both acids if either conc missing

1

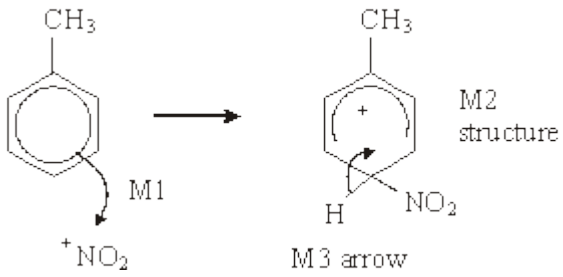
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

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

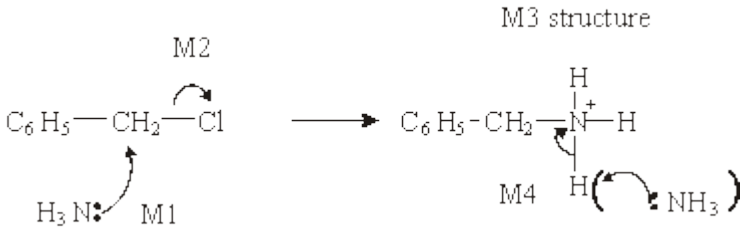
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

1



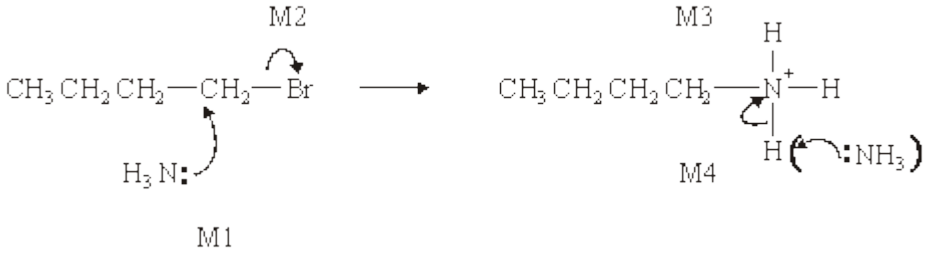
4

[15]

5 B

[1]

6 (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]

7 B

[1]

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

∴ (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

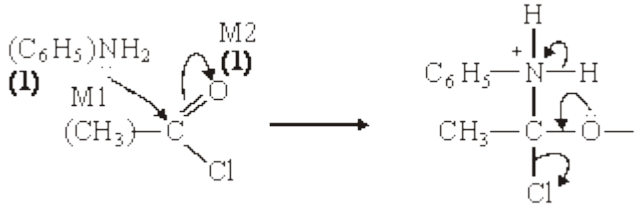
(b) (i) phenylamine weaker **(1)**

if wrong no marks

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

3

(ii) addition – elimination **(1)**



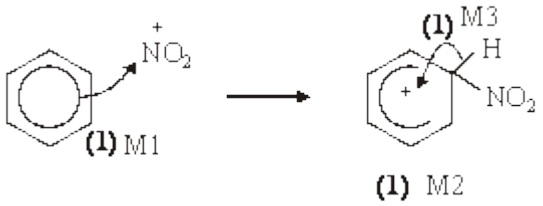
*structure **(1)** M3*
*3 arrows **(1)** M4*

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]

9

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

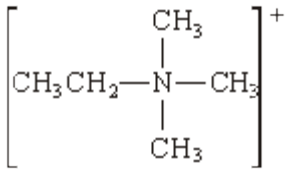
2

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

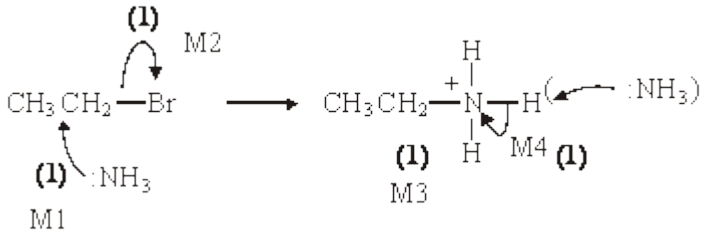
1

nucleophilic substitution

1

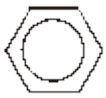
[9]

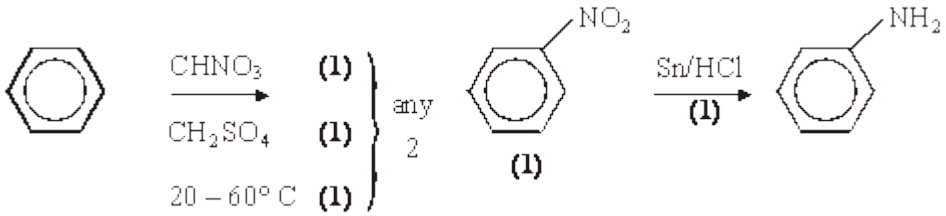
10 (a)



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

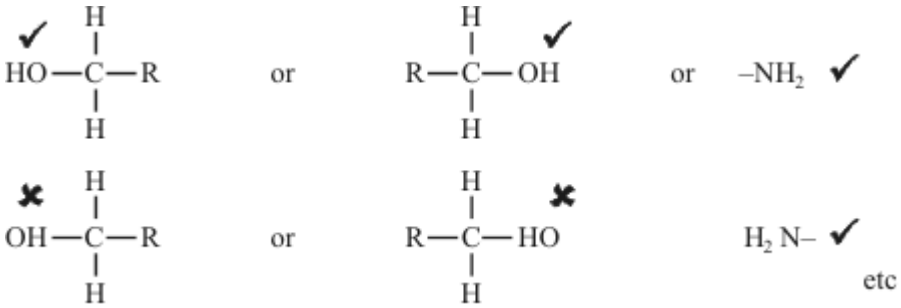
[11]

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



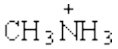
Penalise once per paper

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

11 (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 
or reaction / equilibrium moves to left
or ratio salt / base remains almost constant **(1)**

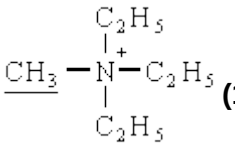
Any 2

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)

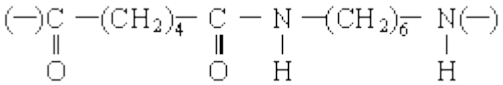
2

[9]

12

(a) (i) hexane-1,6-diamine or 1,6-diaminohexane **(allow ammine)**
or 1,6 hexan(e)diamine **(1)**

(ii)

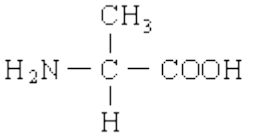


(1)

Allow –CONH–

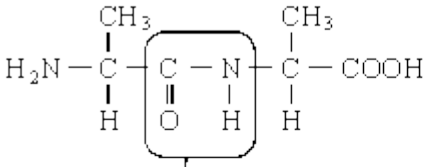
2

(b) (i)



(1)

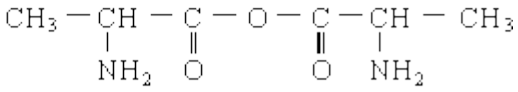
(ii)



(1)

peptide link essential : the rest is consequential on b(i)
(allow CONH)

allow anhydride



2

(c) (i) quaternary ammonium bromide salt **(1)**

(not ion, not compound)

Allow quarternery

(ii) *Reagent*: CH_3Br or bromomethane **(1)**

penalise CH_3Cl but allow excess for any halomethane

Condition: excess (CH_3Br) **(1)**

(iii) nucleophilic substitution **(1)**

4

[8]