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

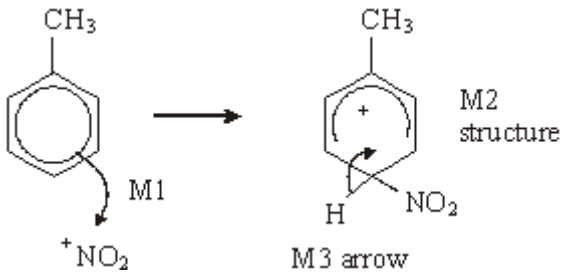
1

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

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

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

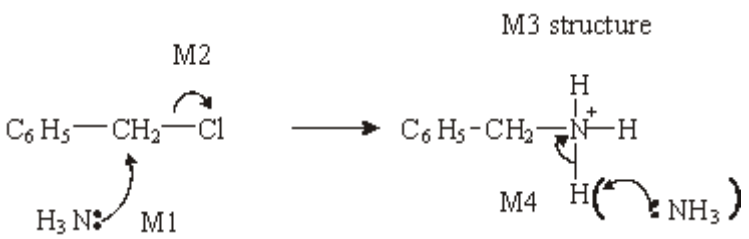
1

Use an excess of ammonia

1

(ii) nucleophilic substitution

1



4

[15]

M3. D

[1]

M4. (a) **M1** Benzene is <u>more stable than cyclohexatriene</u>

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

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

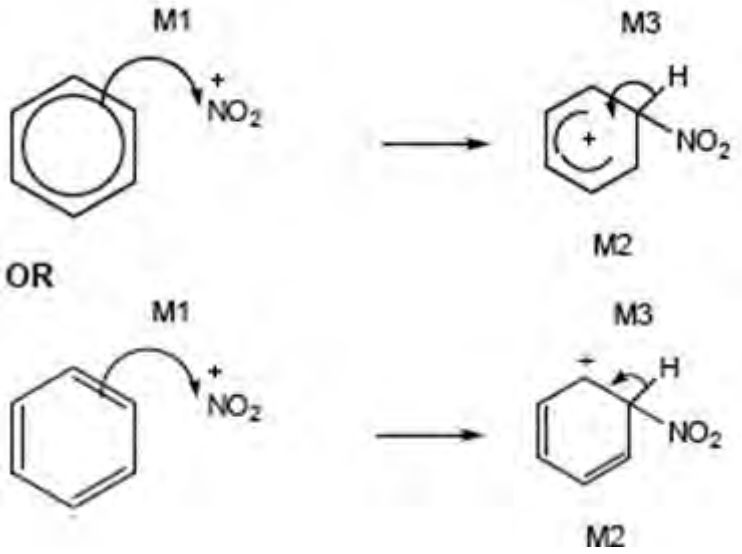
OR via two equations

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

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

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

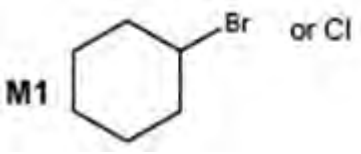
allow M3 arrow independent of M2 structure

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]