M1.(a) (i) 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

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

1

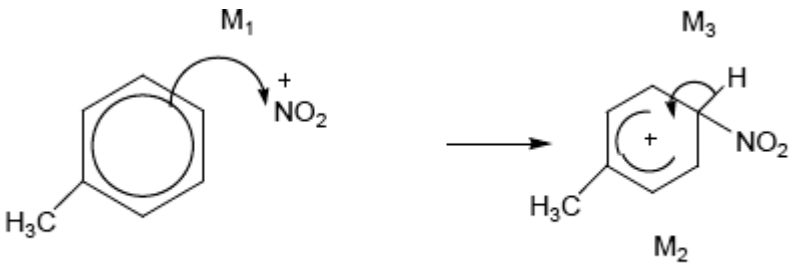
OR $H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

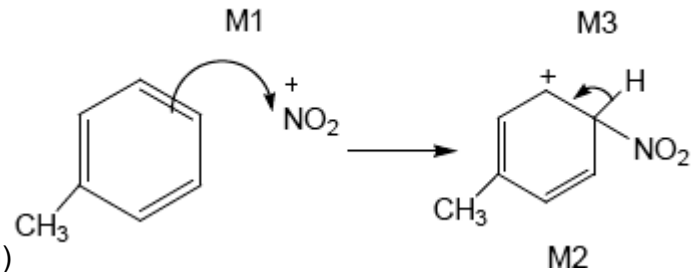
OR via two equations

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

$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$



OR



(ii)

- *ignore position or absence of methyl group in M1 but must be in correct position for M2*
- *M1 arrow from within hexagon to N or <u>+ on N</u>*
- *Allow NO_2^+ in mechanism*
- *Bond to NO_2 must be to 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*
- *+ on H in intermediate loses M2 not M3*

3

(b) 5

1

(c) 2

1

(d) $2C_7H_5N_3O_6 \longrightarrow 5H_2O + 3N_2 + 7C + 7CO$

Or halved

1

[9]

M2. (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

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

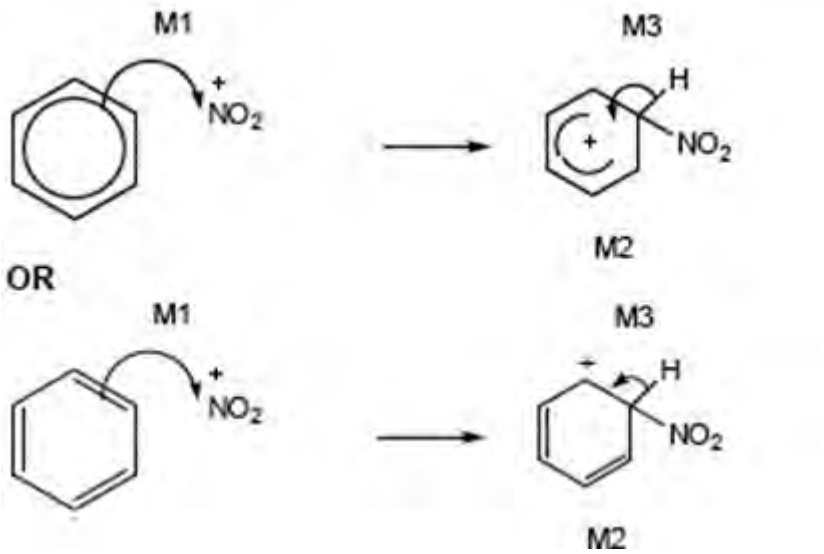
OR via two equations

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

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



M1 arrow from within hexagon to N or + on N

Allow NO_2^+ in mechanism

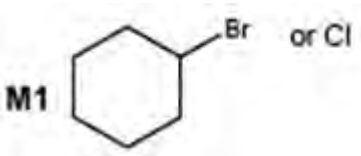
horseshoe must not extend beyond C2 to C6 but can be

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)**

M1



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]

M3. C

[1]

M4. (a) CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride
OR $(CH_3CH_2CO)_2O$ OR propanoic anhydride
penalize contradiction in formula and name e.g. propyl chloride
could score in equation

1

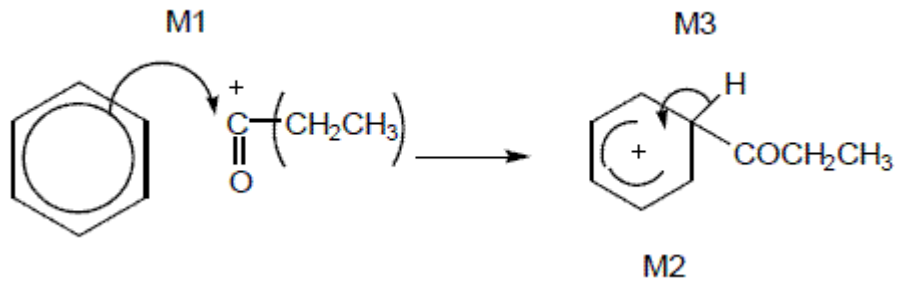
$AlCl_3$ or $FeCl_3$ or names
could score in equation

1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$
Allow RCOCl in equation but penalise above
allow + on C or O in equation

1

(b)



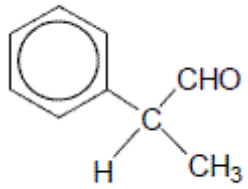
M1 arrow from circle or within it to C or to + on C
Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure

Ignore base removing H in M3

3

(c) Tollens or ammoniacal silver nitrate

1



penalise wrong formula

1

[8]

M5. (a) (i) $C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$

OR

$C_6H_6 + CH_3CH_2CO^+ \rightarrow C_6H_5COCH_2CH_3 + H^+$

allow C_2H_5
penalise C_6H_5–CH_3CH_2CO
allow + on C or O in equation

1

Phenylpropanone

OR ethylphenylketone **OR** phenylethylketone

Ignore 1 in formula, but penalise other numbers

1

$AlCl_3$

can score in equation

1

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$

allow C_2H_5
allow + on C or O in equation

1

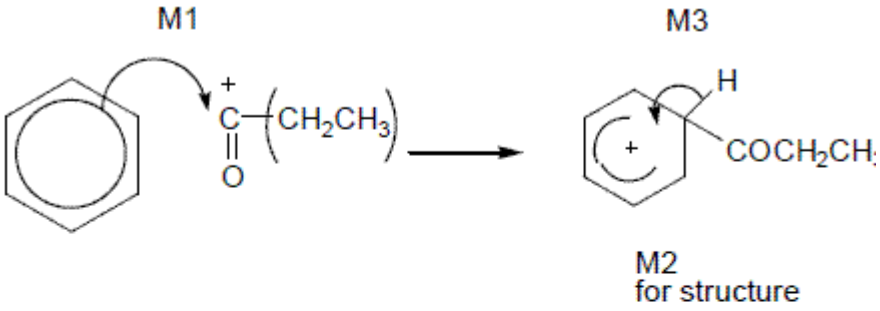
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

1

(ii) electrophilic substitution

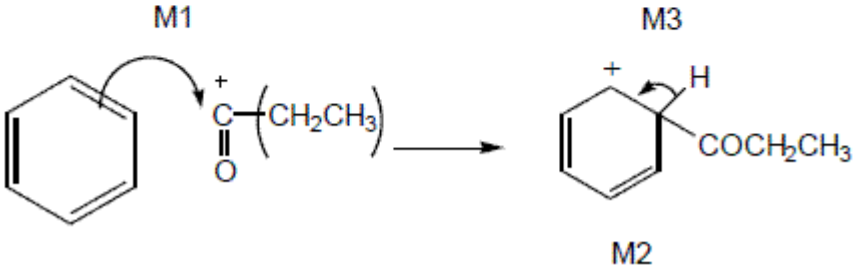
can allow in (a)(i) if no contradiction

1



M2
for structure

OR



M2

M1 arrow from circle or within it to C or to + on C
horseshoe must not extend beyond C2 to C6 but can be smaller
+ not too close to C1
M2 penalise C_6H_5–CH_3CH_2CO (even if already penalized in (a)(i))
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure
ignore base removing H in M3

3

(b) (i) $CH_3CH_2\underline{CHO} + HCN \rightarrow CH_3CH_2CH(OH)CN$ **OR** $C_2H_5CH(OH)CN$

aldehyde must be –CHO brackets optional

1

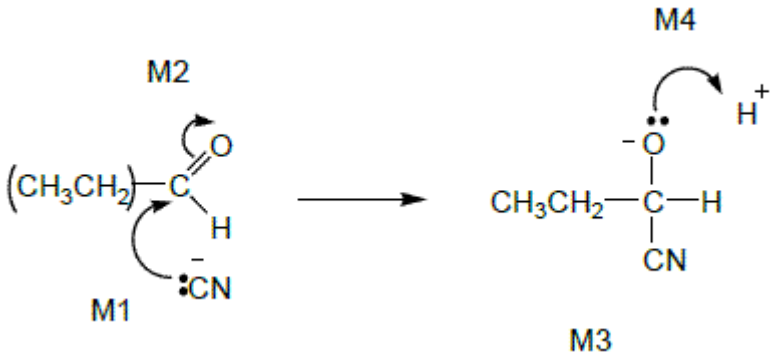
2-hydroxybutanenitrile **OR** 2-hydroxybutan<u>o</u>nitrile

no others

1

(ii) nucleophilic addition

1



M1 includes lp and arrow to Carbonyl C and minus charge (on either C or N)
Not allow M2 before M1, but allow M1 to C^+ after non-scoring carbonyl arrow
Ignore δ+, δ– on carbonyl group, but if wrong way round or full + charge on C lose M2
M3 for correct structure including minus sign. Allow C_2H_5
M4 for lp and curly arrow to H^+

4

(iii) (propanone) slower ***OR*** <u>propanal</u> faster

1

inductive effects of alkyl groups
OR
C of C=O less δ+ in propanone
OR
alkyl groups in ketone hinder attack
OR
easier to attack at end of chain

if wrong, no further marks

1

[18]