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

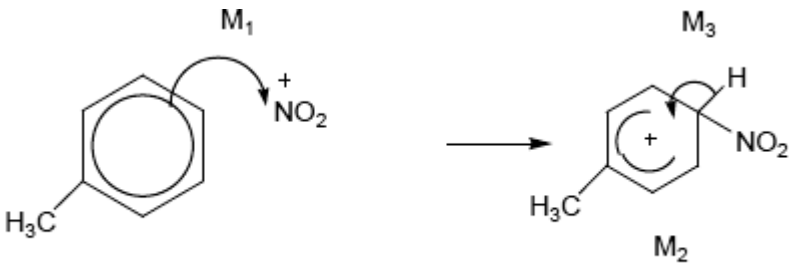
OR $H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

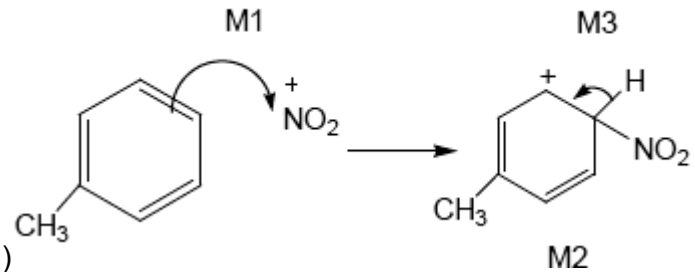
OR via two equations

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

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



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 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

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

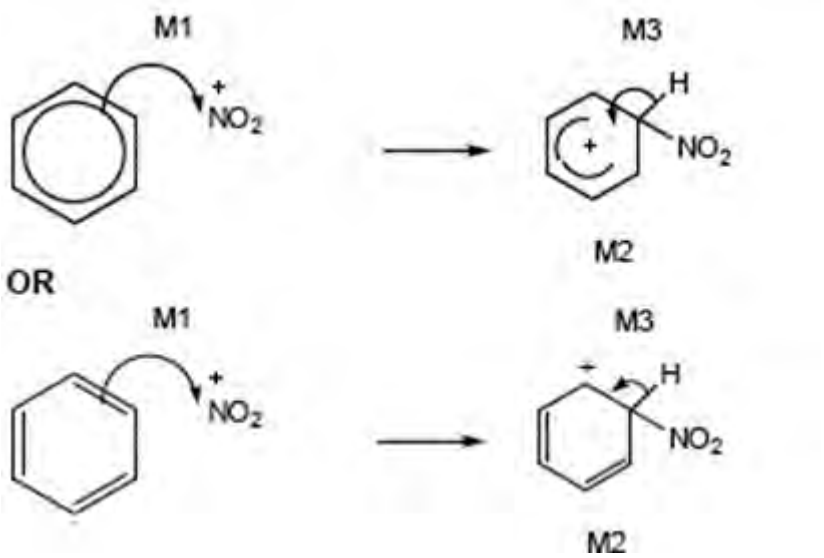
OR via two equations

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

$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



M1 arrow from within hexagon to N or + on N

Allow NO_2^+ in mechanism

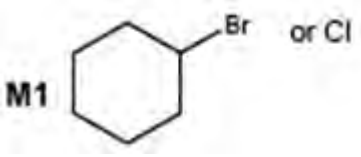
horseshoe must not extend beyond C2 to C6 but can be

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)**

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

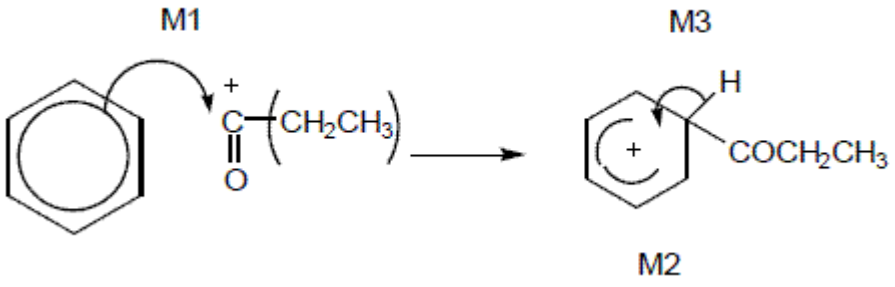
$AlCl_3$ or $FeCl_3$ or names
could score in equation

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)



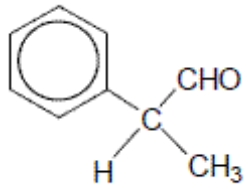
M1 arrow from circle or within it to C or to + on C
Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1
M3 arrow into hexagon unless Kekule
allow M3 arrow independent of M2 structure

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

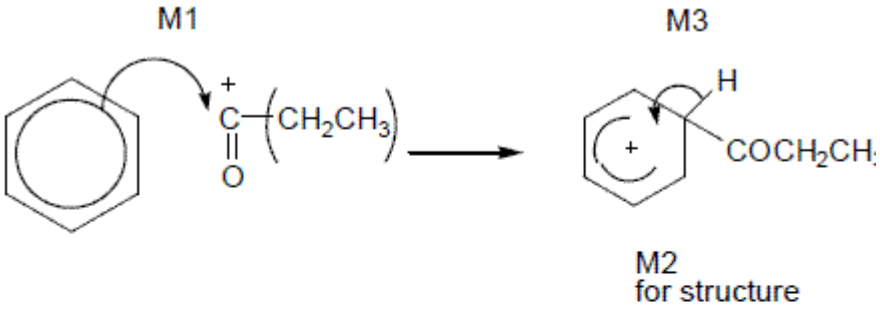
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

1

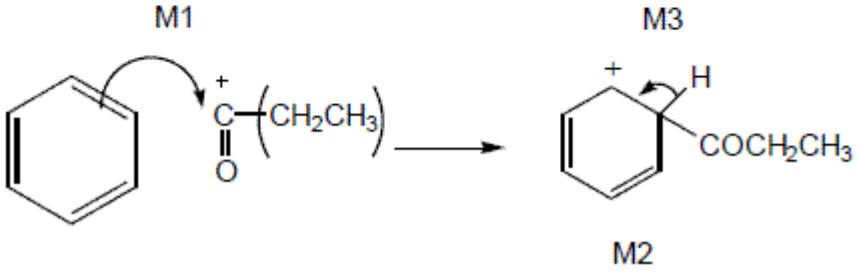
(ii) electrophilic substitution

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

1



OR



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 → $CH_3CH_2CH(OH)CN$ **OR** $C_2H_5CH(OH)CN$

aldehyde must be –CHO brackets optional

1

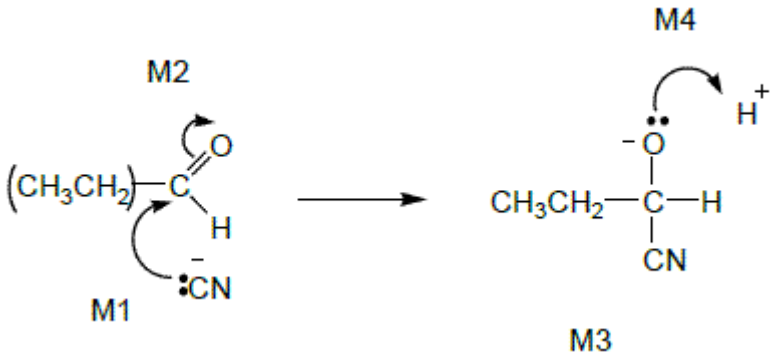
2-hydroxybutanenitrile **OR** 2-hydroxybutan<u>o</u>nitrile

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]