TOPIC 18 TEST MS

1. (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

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

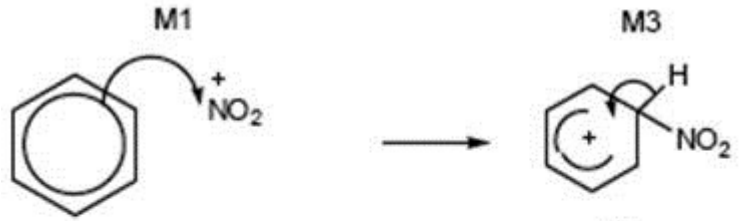
OR via two equations

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

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



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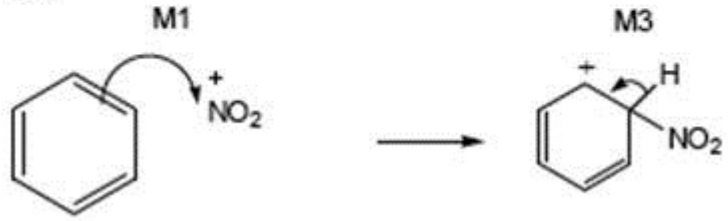


M1 arrow from within hexagon to N or + on N

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

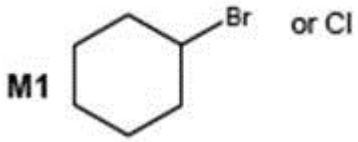
ignore base removing H in M3

+ 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 <u>pair on N</u>

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.

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.
If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change

Ignore 'clear', 'nothing'.
Allow colour fades slowly.
Allow 'nvc' for no visible change.

1

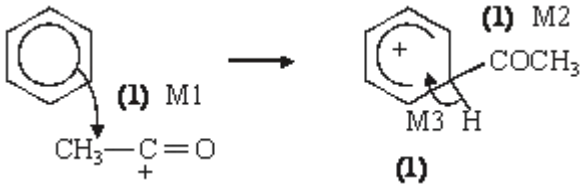
cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[3]

3. (i) ([]) CH_3CO ([])$^+$ **(1)**

(ii)



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Notes

extra curly arrows are penalised

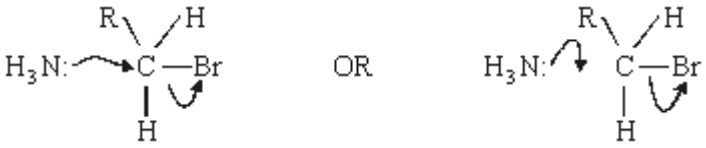
(i) allow formula in an "equation"(balanced or not)
be lenient on the position of the + on the formula

(ii) for M1 the arrow must go to the C or the + on the C
don't be too harsh about the horseshoe, but + must not be close to the saturated C
M3 must be final step not earlier; allow M3 even if structure (M2) is wrong

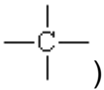
[4]

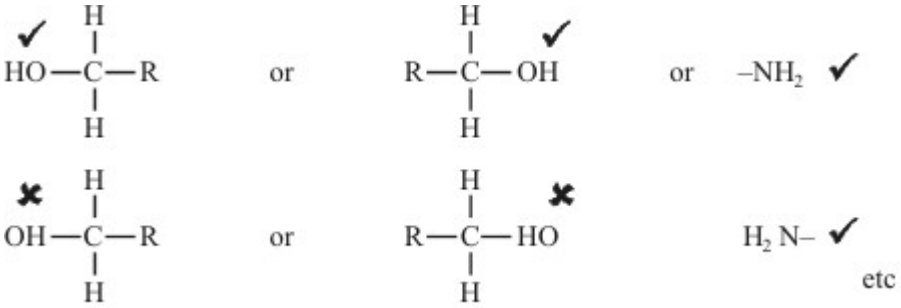
Organic points

(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

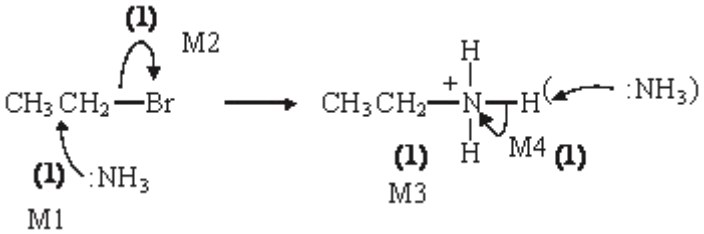
penalise sticks (i.e. ) once per paper



Penalise once per paper

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

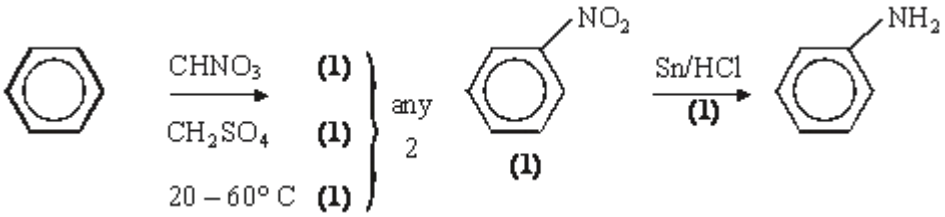
4. (a)



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)**



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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]

5. (a) Ammonia is a nucleophile
Allow ammonia has a lone pair.

1

Benzene repels nucleophiles
Allow (benzene) attracts / reacts with electrophiles.
OR *benzene repels electron rich species or lone pairs.*
OR *C–Cl bond is short / strong / weakly polar.*

1

(b) H_2 / Ni **OR** H_2 / Pt **OR** Sn / HCl **OR** Fe / HCl
Ignore dil / conc of HCl.
Ignore the term 'catalyst'.
Allow H_2SO_4 with Sn and Fe but not conc.
Ignore NaOH following correct answer.
Not $NaBH_4$ nor $LiAlH_4$.

1

(c) <u>conc HNO_3</u>

<u>conc H_2SO_4</u>

1

If either or both conc missed can score 1 for both acids.

1

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

OR using two equations

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

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

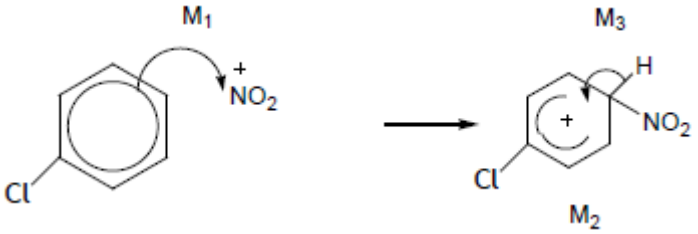
Allow 1:1 equation.

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

1

(d) <u>Electrophilic substitution</u>

1



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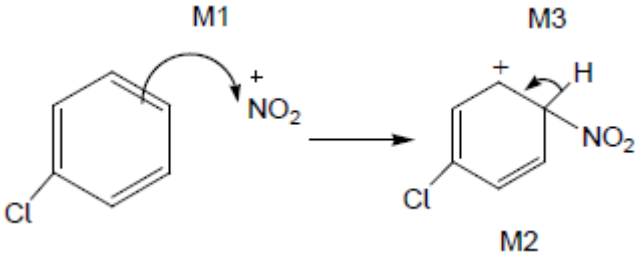

- *Ignore position or absence of Cl in M1 but must be in correct position for M2.*
- *M1 arrow from within hexagon to N or <u>+ on N</u>.*
- *Allow NO_2^+ in mechanism.*
- *Bond to NO_2 must be to N for structure mark M2.*
- *Gap in horseshoe must be centered around correct carbon (C1).*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6).*
- *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

[10]

6. A

[1]

7. B

[1]

8. C

[1]