AROMATIC CHEMISTRY TEST Answers

1. (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

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

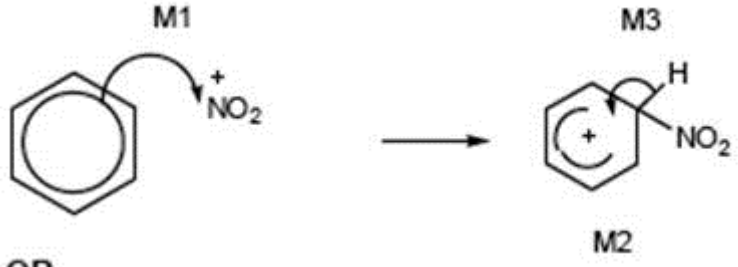
OR via two equations

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

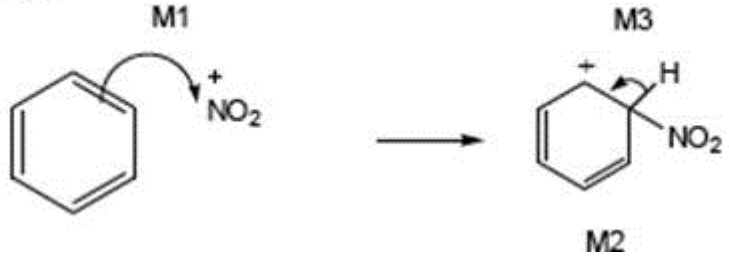
$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

Allow + anywhere on NO_2^+

1



OR



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

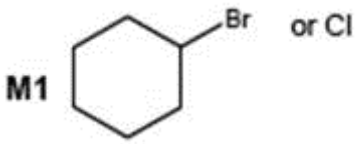
allow M3 arrow independent of M2 structure

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

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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	no reaction / colour remains / no (visible) change

	(visible) change	

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

1

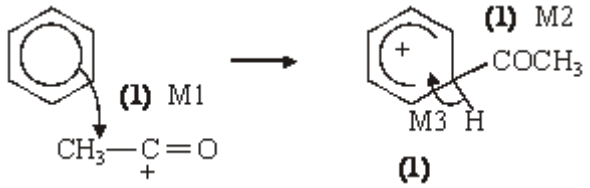
cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[3]

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

(ii)



4

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

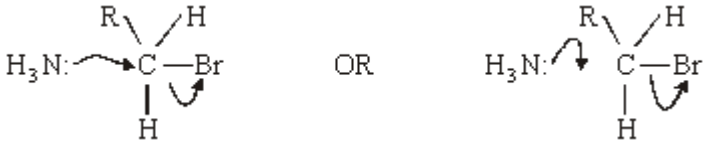
(ii) for M1 the arrow must go to the C or the + on the C
don't be too harsh about the horseshoe, but + must not be close to the saturated C
M3 must be final step not earlier; allow M3 even if structure (M2) is wrong

[4]

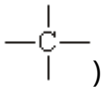
Organic points

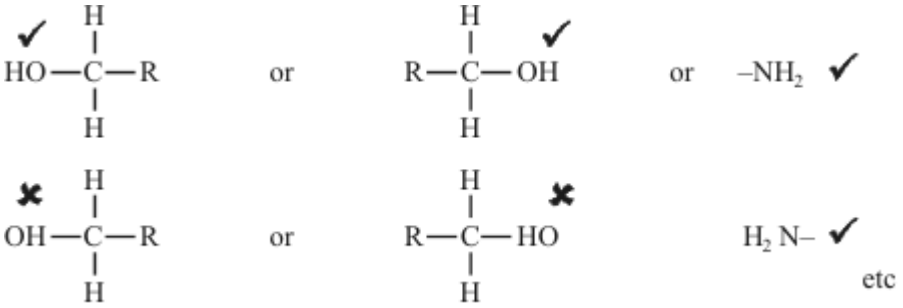
(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space

e.g.



(2) Structures

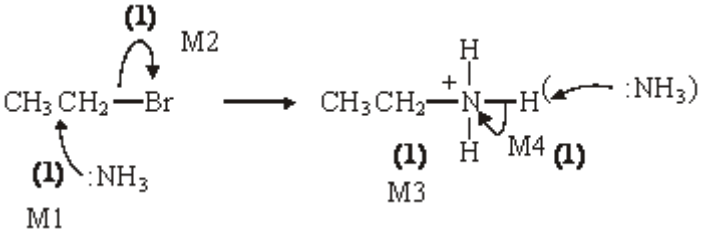
penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH_3– or $-CH_3$ or  or CH_3
or H_3C–

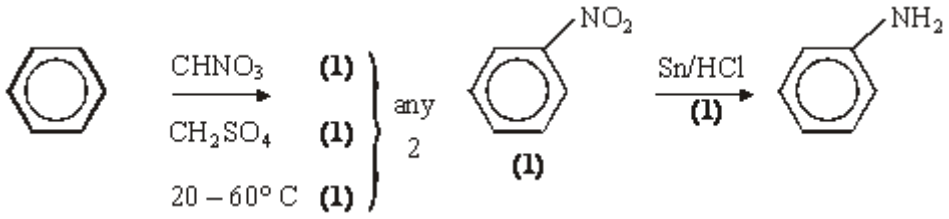
4. (a)



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

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

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

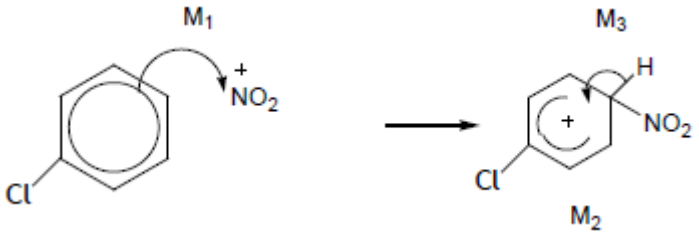
Allow 1:1 equation.

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

1

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

1



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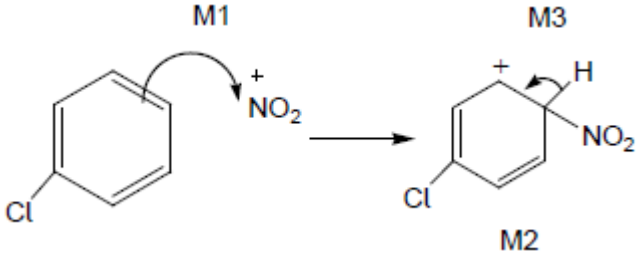

- *Ignore position or absence of Cl in M1 but*

must be in correct position for M2.

- *M1 arrow from within hexagon to N or + on N.*
- *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]