A-Level Chemistry

Structure of Benzene

Mark Scheme

Time available: 68 minutes
Marks available: 66 marks

1.

(a) (3 x 612) + (3 x 348) + (6 x 412) = 5352

For LHS

M1

(6 x 715) + (6 x 218) = 5598

For RHS

M2

ΔH_2 = M2 - M1 - 83 = +163 kJ mol^{-1}

M3

(b) (π) electrons delocalised

1

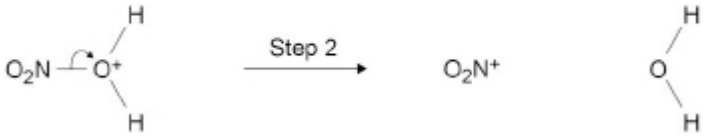
(c) M1 Electrophilic substitution

1

M2 for a lone pair and two curly arrows

1

M3 for a curly arrow from the bond to the O

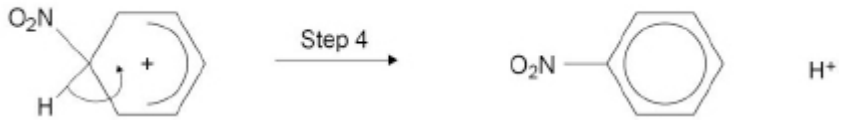


1

M4 for a curly arrow from inside the hexagon to the N or + on the N

1

M5 curly arrow from the bond back into the hexagon



1

[9]

2.

This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.	
Level 3 5-6 marks	All stages are covered and the explanation of each stage is generally correct and virtually complete. Answer communicates the whole process coherently and shows a logical progression from stage 1 and stage 2 to stage 3. Completely correct use of sign and language in Stage 3.
Level 2 3-4 marks	All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete. Answer is mainly coherent and shows a progression through the stages. Some steps in each stage may be incomplete. Some errors in use of sign and language in Stage 3.
Level 1 1-2 marks	Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR only one stage is covered but the explanation is generally correct and virtually complete. Answer includes some isolated statements but these are not presented in a logical order or show confused reasoning.
Level 0 0 marks	Insufficient correct chemistry to gain a mark.

Indicative chemistry content

Stage 1 Bonding

1a) Each C has three (covalent) bonds

1b) Spare electrons (in a p orbital) overlap (to form a π cloud)

1c) delocalisation

Stage 2 Shape

2a) Planar

2b) Hexagon/6 carbon ring/120° bond angle

2c) C–C bonds equal in length / C–C bond lengths between single and double bond

Stage 3 Stability

3a) Expected ΔH^{o} hydrogenation of cyclohexatriene = –360 kJ mol^{-1}

3b) ΔH^{o} hydrogenation benzene (is less exothermic) by 152 kJ mol^{-1}

3c) Benzene lower in energy than cyclohexatriene / Benzene is more stable

6

(b) Value within range –239 to –121

If outside range including positive values CE=0

1

Double bonds separated by one single bond / alternating (or shown in structure)

The wording 'close enough to allow delocalisation' would score M2 and M3

1

Allows some delocalisation/overlap of p orbitals

Ignore reference to hydration here

1

[9]

3.

(a) (i) 3(-120) − (-208) = -152
OR
3(120) − 208 = 152 (kJ mol^{-1})

Must show working and answer and maths must be correct, but ignore sign

1

(ii) Electrons delocalised OR delocalisation (QOL)
OR
allow reference to resonance (QOL)

1

(b) x, y, w

Must be in this order

1

(c) (i) -240 (kJ mol^{-1})

Must have minus sign

1

(ii) between -239 and -121 (kJ mol^{-1})

Must have minus sign

1

(iii) Must specify which diene:

Proximity − for 1,3 C=C bonds are close together

allow converse for 1,4 diene

M1

1

Delocalisation − for 1,3 some delocalisation
OR
some overlap of electrons, π clouds or p orbitals

allow converse for 1,4 diene

M2 **1**

some extra stability for the 1,3- isomer

M3 **1**

[8]

4. (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 ΔHº hydrogenation of C_6H_6 is 3(–120)

= –360 kJ mol^{-1}

Allow in words e.g. expected ΔHº hydrog is three times the ΔHº hydrog of cyclohexene

1

M3 Actual ΔHº 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

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

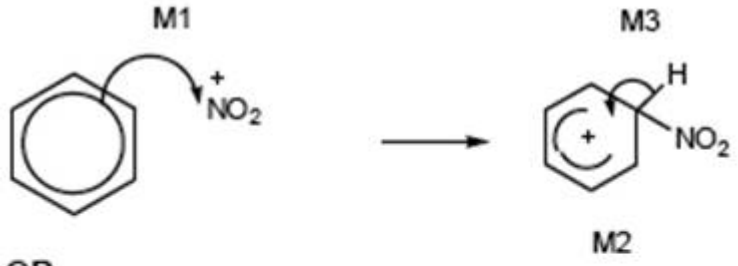
OR via two equations

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

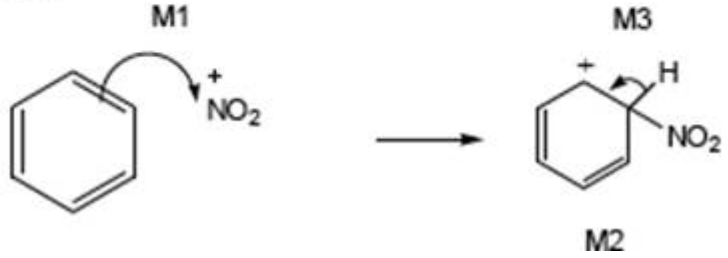
$H_2NO_3+ \rightarrow NO_2^+ + H_2O$

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

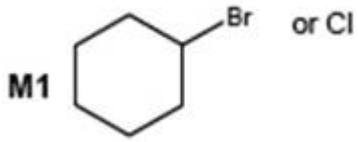
allow M3 arrow independent of M2 structure

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)**

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]

5. (a) Cyclohexane evolves 120 kJ mol^{-1}

∴ (expect triene to evole) 360 kJ mol^{-1} **(1)** or 3 × 120

360 – 208 = 152 kJ **(1)** NOT 150

152 can score first 2

*QofL: benzene lower in energy / <u>more</u> (stated) stable **(1)***

Not award if mentions energy required for bond breaking

*due to <u>delocalisation</u> **(1)** or explained*

4

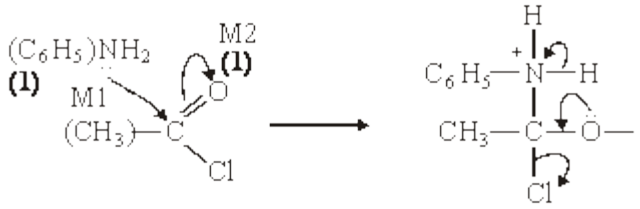
(b) (i) phenylamine weaker **(1)**

if wrong no marks

lone pair on N (less available) **(1)**
delocalised into ring **(1)** or "explained"

3

(ii) addition – elimination **(1)**



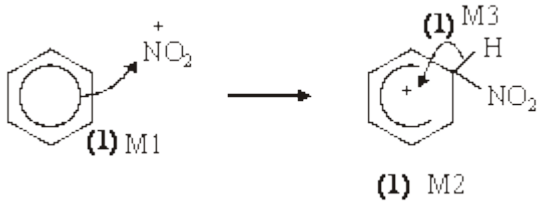
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

(iii) conc HNO_3 **(1)**
conc H_2SO_4 **(1)**

$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$ **(1)**



6

(iv) peptide / amide **(1)**

NaOH (aq) **(1)**

HCl conc or dil or neither
H_2SO_4 dil NOT conc
NOT just H_2O

2

Notes

(a)
- 360 or 3 × 120 or in words **(1)**;
- 152 NOT 150 **(1)**; (152 can get first two marks)
- **Q of L** benzene <u>more</u> stable but not award if ΔH values used to say that more energy is required by benzene for hydrogenation compared with the triene or if benzene is only compared with cyclohexene **(1)**;
- delocalisation or explained **(1)**

(b) (ii) or N-phenylacetamide or acetanilide
mechanism: if shown as substitution can only gain M1
if CH_3CO+ formed can only gain M1
lose M4 if Cl^- removes H^+
be lenient with structures for M1 and M2 but must be correct for M3
 alone loses M2

(iii) **No marks for name of mechanism in this part**
if conc missing can score one for both acids (or in equation)
allow two equations

allow $HNO_3 + H_2SO_4 \rightarrow NO^{2+} + HSO_4^- + H_2O$
ignore side chain in mechanism even if wrong
arrow for M1 must come from niside hexagon
arrow to NO_2^+ must go to N but be lenient over position of +
+ must not be too near "tetrahedral" Carbon
horseshoe from carbons 2-6 but don't be too harsh

(iv) reagent allow NaOH
HCl conc or dil or neither
H_2SO_4 dil or neither but not conc
not just H_2O

[21]