AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.3.10 AROMATIC CHEMISTRY

SCORE	PERCENTAGE
/76	%

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Q1.

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}

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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]

Q2.

A

[1]

Q3.

(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)
ORallow 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

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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]

Q4.

(a) Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid

Allow H_2 (Ni / Pt) but penalise wrong metal

But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH

1

Equation must use molecular formulae

$C_6H_4N_2O_4 + 12\,[H]$

12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2

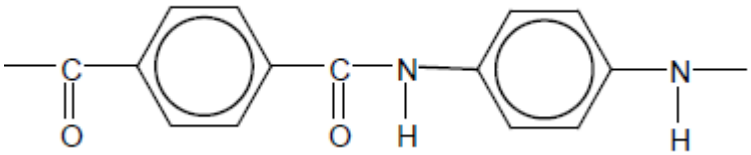
1

$\rightarrow C_6H_8N_2 + 4H_2O$

Allow .... + $6H_2$ if H_2 / Ni used

Allow −CONH− or −COHN− or $-C_6H_4-$

1



Mark two halves separately: lose 1 each for

- *error in diamine part*
- *error in diacid part*
- *error in peptide link*
- *missing trailing bonds at one or both ends*
- *either or both of H or OH on ends*

Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal

NOT Sn / HCl, $NaBH_4$ etc.

1

CH_2

1

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In benzene 120°

1

In cyclohexane 109° 28’ or 109½°

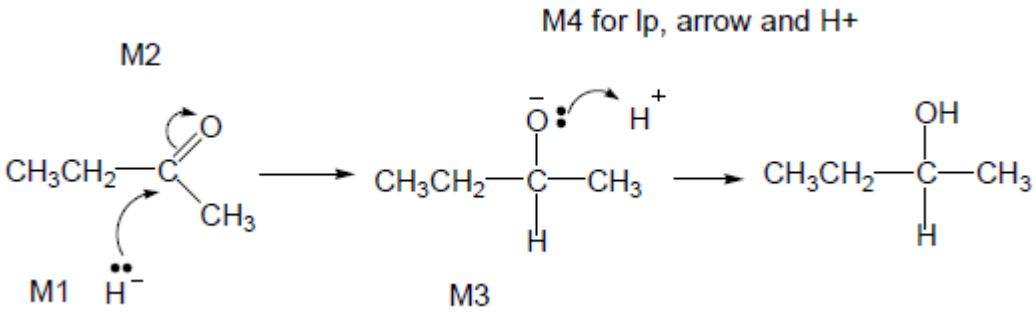
Allow 108° - 110°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

1



- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *M3 is for correct structure including minus sign but lone pair is part of M4*
- *Allow C_2H_5*
- *M1 and M4 include lp and curly arrow*
- *Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)*

4

(ii) M1 Planar C=O (bond / group)

Not just planar molecule

1

M2 Attack (equally likely) from either side

Not just planar bond without reference to carbonyl

1

M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely

1

[17]

Q5.

(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)

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= –360 kJ mol^{-1}

Allow in words e.g. expected ΔH^{e} hydrog is three times the ΔH^{e} hydrog of cyclohexene

1

M3 Actual ΔH^{e} 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

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

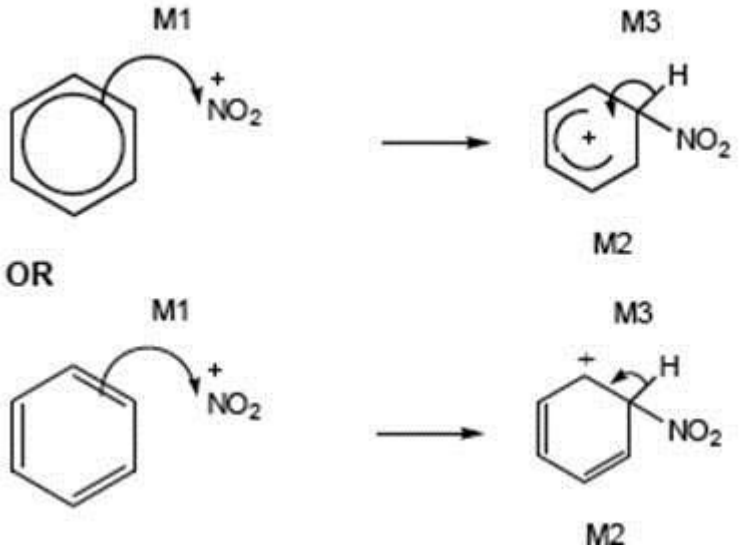
OR via two equations

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

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

Allow + anywhere on NO_2^+

1



M1 arrow from within hexagon to N or + on N

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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

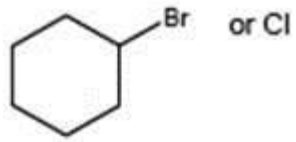
ignore base removing H in M3

+ 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]

Q6.

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

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$\therefore$ (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

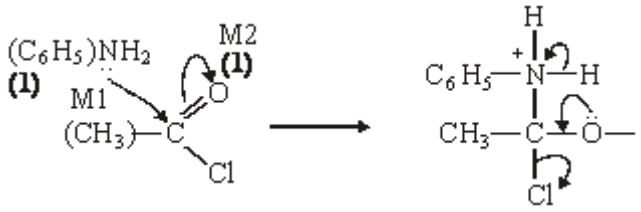
(b) (i) phenylamine weaker **(1)**

if wrong no marks

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

3

(ii) addition – elimination **(1)**



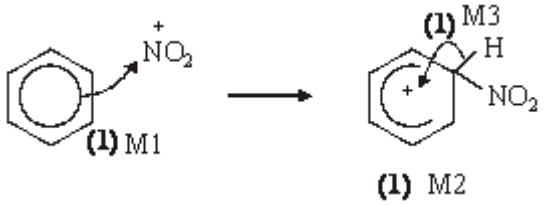
*structure **(1)** M3*
*3 arrows **(1)** M4*

N-phenyl ethanamide **(1)**

6

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

$HNO_3 + 2H_2SO_4 \rightarrow {}^{+}NO_2 + H_3O^+ + 2HSO_4^-$ **(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)

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- **Q of L** benzene more 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]

Q7.

A

[1]

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Q1.

(a) All but the weakest students were able to calculate the expected enthalpy of hydrogenation of –360 kJ mol^{-1} and the consequent 152 kJ mol^{-1} extra stability of benzene and explain this in terms of electron delocalisation. Most students knew that carbon formed three bonds but only a few were able to discuss that the extra outer shell p electrons overlap to form the pi cloud. Shape was less commonly discussed, although many noted that the molecule was planar. Sadly, although Level 3 answers were provided by 15.3% of the students, only a third of these gained full marks as their explanations often contained errors such as “hydration” for hydrogenation, or unclear discussion about bond breaking during the addition of hydrogen.

(b) This question proved challenging. Some students gave a wrong value that was more exothermic than –240 kJ mol^{-1}. Of those who gave a suitable value, many were unable to explain it in terms of some extra stability due to delocalisation. Only 8.7% of students were able to justify this in terms of alternate single and double bonds forming a conjugated system and so gain full marks.

Q3.

The straightforward question in part (a)(i) was well answered, although some students did not gain the mark as a result of failing to use all three pieces of data or of writing incorrect maths such as –360 – (–208) = +152. As expected part (a)(ii) was high scoring but part (b) was answered less well. In part (c) the data was often referred to as hydration and also as energy required to break the bonds rather than energy released as cyclohexane was formed.
The value for 1,4-cyclohexadiene in part (c)(i) was usually correct, but the possibility of partial delocalisation in the 1,3 diene in part (c)(ii) was not at all well understood. The predicted enthalpy of hydrogenation of the 1,3-diene was often given as the same as the 1,4-diene. In part (c)(iii) a mark for noting that the C=C bonds were closer in the 1,3-diene was often gained. However many students then went on to say in error that adjacent C=C bonds repel and so the 1,3-diene is less stable. It was rare to see a student apply their knowledge of delocalisation in benzene to the 1,3-diene, to deduce that partial delocalisation can occur here and, as with benzene, this causes some extra stability and so the enthalpy of hydrogenation is less exothermic than -240 $kJmol^{-1}$.

Q4.

In part (a), many students thought $NaBH_4$ or $LiAlH_4$ could be used as the reducing agent. Most did not give the molecular formulae in the equation but could balance it correctly; the repeating unit of the polymer was very well done.

Similarly, in part (b), $NaBH_4$ was often suggested as the reducing agent and the empirical formula was frequently wrong. Students found the bond angles difficult, with many failing to deduce that there is a tetrahedral arrangement around a C atom in cyclohexane and appearing simply to guess any angle. Only the most able scored both marks for the bond angles.

There was a good spread of marks in the mechanism with over 40% gaining full marks. In part (c)(ii), most realised that the product was a racemic mixture and that it was produced as a result of attack on the ketone from both sides, but often this was thought to be by an electrophile or an H^+ ion. Some thought that a carbocation intermediate was attacked.

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Q5.

In part (a), although most candidates scored at least half marks, some candidates did not use the data as requested. Some answers also referred to cyclohexatriene but went on to talk about one double bond.

Part (b) was well done, especially the mechanism. The most common errors were to omit *concentrated* for either or both acids or to omit the positive charge on the $H_2NO_3^+$ when writing two equations.

The synthesis in part (c) was a stretch and challenge question and was, as expected, very discriminating. There were some excellent answers but also many which failed to score.

Many candidates were unable to identify V and those who did often named it as a halobenzene even if they drew a correct structure. Preparation of the amine by nucleophilic substitution using an excess of ammonia was credited in Reaction 4 even if the answers to V and Reaction 3 were wrong.

A surprising number of candidates thought a base was a proton donor. Some otherwise good answers did not score as they failed to mention the lone pair on the nitrogen atom.

Many also simply stated that amine U contained delocalised electrons but failed to explain how involvement of the lone pair on nitrogen with these electrons lowered the base strength.

Q6.

In part (a), not all candidates noted the requirement in the question to “Use the data”. The numerical difference of 152 kJ mol^{-1} between the expected enthalpy of hydrogenation of -360 kJ mol^{-1} and the actual value of –208 kJ mol^{-1} was rarely noted. Weaker candidates also thought that the data given was of the energy required to cause the reaction, rather than that evolved in the reaction. In part (b), weaker candidates muddled the expected addition-elimination reaction of an acid chloride and an amine with a Friedel Craft’s substitution in the benzene ring and frequently gained no marks for the section. The correct name for the product, N-phenylethanamide was rarely seen. Part (c) was better answered; most candidates were able to discuss nitration correctly and the mechanism was better answered than that in part (b)(ii). The amide or peptide link was not always named correctly in part (iv) and many did not state that acidic or alkaline hydrolysis is required to break the bond.

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