

AQA A-LEVEL CHEMISTRY • 7405

CHEMISTRY



EXAM QUESTION PACK

3.3.10 AROMATIC CHEMISTRY

SCORE

/76

PERCENTAGE

%

STEMUP

These questions belong to AQA, not to us.

The examination questions, mark schemes and examiner reports in this pack were written and published by AQA. They are past assessment materials, reproduced here so that students can revise from them.

What we do not own

STEMUP is not affiliated with AQA and does not own, and makes no claim to own, any of the question, mark scheme or examiner report material in this pack. AQA has not endorsed, approved or been involved in the production of it. AQA and the qualification titles used here belong to their respective owners and appear for identification only.

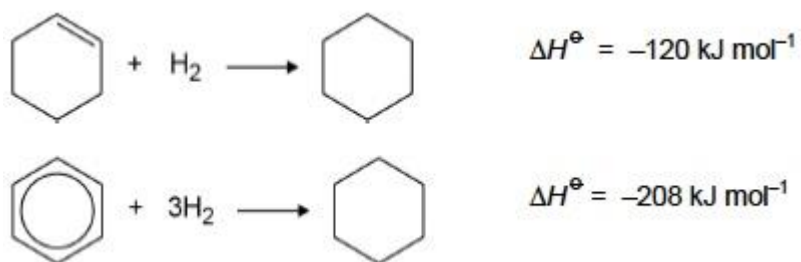
Where to find the originals

AQA publishes its past papers, mark schemes and examiner reports free of charge. Always check the current specification at aqa.org.uk before you revise, because content and wording can change between series.

If you hold the rights to any material in this pack and would like it amended or removed, contact admin@stemup.co.uk and we will act on it.

Q1.

Data about the hydrogenation of cyclohexene and of benzene are given.



- (a) Explain the bonding in and the shape of a benzene molecule.
Compare the stability of benzene with that of the hypothetical cyclohexa-1,3,5-triene molecule.
Use the data in your answer.

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and extend across the width of the page. There are no margins, text, or other markings on the paper.

(6)

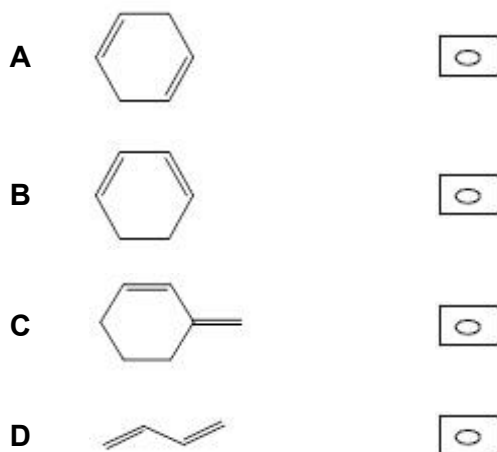
- (b) The enthalpy of hydrogenation of cyclohexa-1,3-diene is **not** exactly double that of cyclohexene.

Suggest a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene and justify your value.

(3)
(Total 9 marks)

Q2.

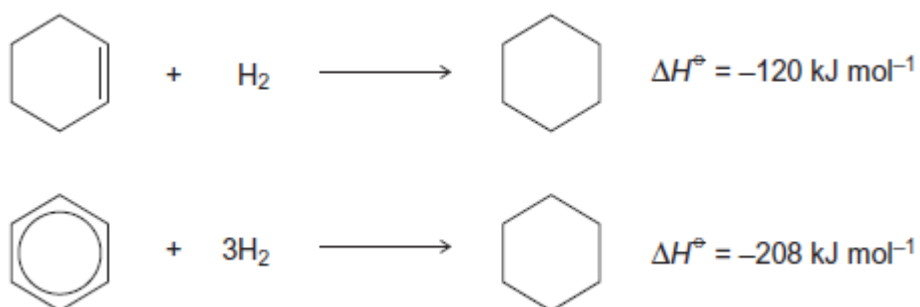
Use your understanding of the bonding in benzene to identify the compound that has the most exothermic enthalpy of hydrogenation.



(Total 1 mark)

Q3.

Equations for the hydrogenation of cyclohexene and of benzene, together with the enthalpies of hydrogenation, are shown.



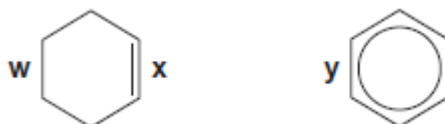
- (a) (i) Use these data to show that benzene is 152 kJ mol^{-1} more stable than the hypothetical compound cyclohexa-1,3,5-triene.

(1)

- (ii) State, in terms of its bonding, why benzene is more stable than cyclohexa-1,3,5-triene.

(1)

- (b) Three carbon-carbon bonds are labelled on the structures shown. These bonds are of different lengths.



Write the letters **w**, **x** and **y** in order of **increasing** bond length.

(1)

- (c) The structures of two cyclic dienes are shown.



- (i) Use the enthalpy of hydrogenation data given opposite to calculate a value for the enthalpy of hydrogenation of cyclohexa-1,4-diene.

(1)

- (ii) Predict a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene.

(1)

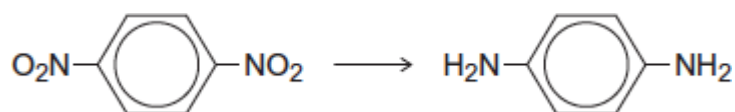
- (iii) Explain your answers to part (i) and part (ii) in terms of the bonding in these two dienes.

(3)
(Total 8 marks)

Q4.

Each of the following conversions involves reduction of the starting material.

- (a) Consider the following conversion.



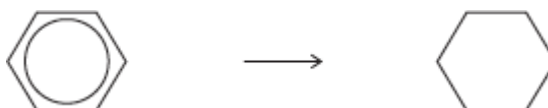
Identify a reducing agent for this conversion.

Write a balanced equation for the reaction using molecular formulae for the nitrogen-containing compounds and [H] for the reducing agent.

Draw the repeating unit of the polymer formed by the product of this reaction with benzene-1,4-dicarboxylic acid.

(5)

- (b) Consider the following conversion.



Identify a reducing agent for this conversion.

State the empirical formula of the product.

State the bond angle between the carbon atoms in the starting material and the bond angle between the carbon atoms in the product.

(4)

- (c) The reducing agent in the following conversion is NaBH_4



- (i) Name and outline a mechanism for the reaction.

Name of mechanism _____

Mechanism

(5)

- (ii) By considering the mechanism of this reaction, explain why the product formed is optically inactive.

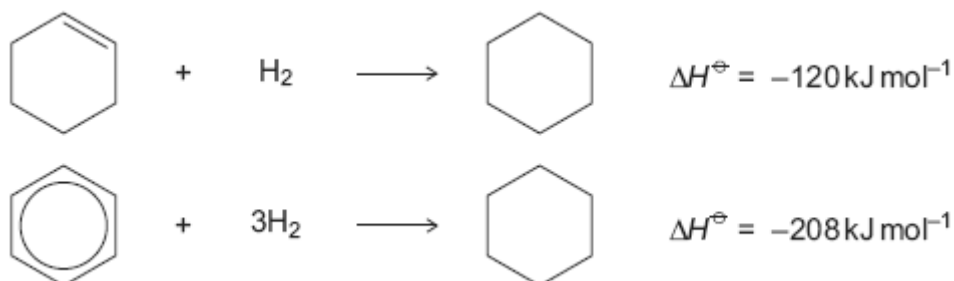
(3)

(Total 17 marks)

Q5.

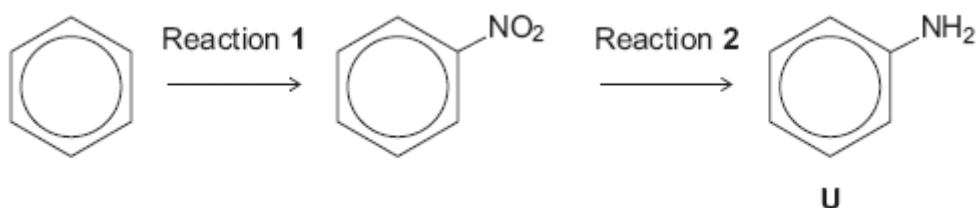
The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

- (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



(4)

- (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



The mechanism of Reaction 1 involves attack by an electrophile.

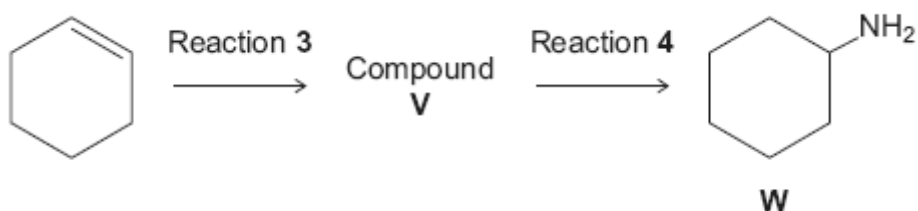
Give the reagents used to produce the electrophile needed in Reaction 1.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

(6)

- (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

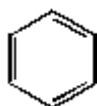
Equations and mechanisms with curly arrows are **not** required.

(6)

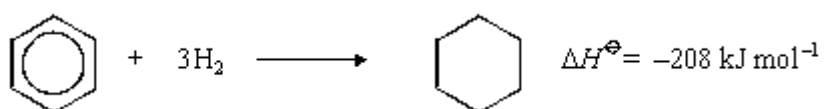
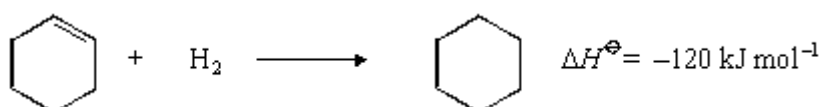
- (d) Explain why amine **U** is a weaker base than amine **W**.

Q6.

- (a) Use the following data to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.

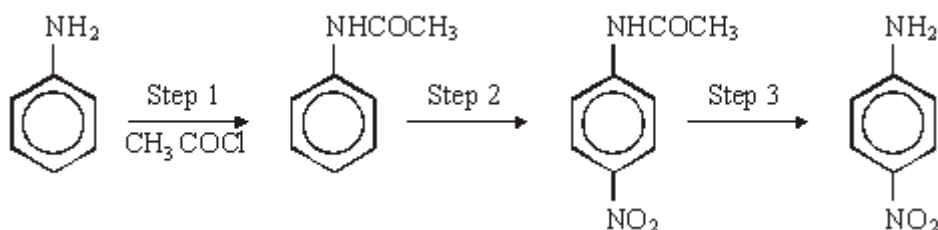


Give a reason for this difference in stability.



(4)

- (b) Consider the following reaction sequence which starts from phenylamine.



- (i) State and explain the difference in base strength between phenylamine and ammonia.

(3)

- (6)**

-
-
-
-
-
-

(6)

- (iv) Name the type of linkage which is broken in Step 3 and suggest a suitable reagent for this reaction.

(2)

(Total 21 marks)

Q7.

Which one of the following does **not** contain any delocalised electrons?

- A** poly(propene)
- B** benzene
- C** graphite
- D** sodium

(Total 1 mark)

Mark schemes

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° hydrogenation of cyclohexatriene = -360 kJ mol^{-1}
- 3b) ΔH° 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]

Q2.

A

[1]

Q3.

(a) (i) $3(-120) - (-208) = -152$

OR

$3(120) - 208 = 152 \text{ (kJ mol}^{-1}\text{)}$

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) $-240 \text{ (kJ mol}^{-1}\text{)}$

Must have minus sign

1

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

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]

Q4.

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

Ignore subsequent use of NaOH

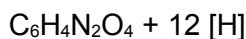
Ignore reference to Sn as a catalyst with the acid

Allow H_2 (Ni / Pt) but penalise wrong metal

But NOT NaBH_4 LiAlH_4 Na / $\text{C}_2\text{H}_5\text{OH}$

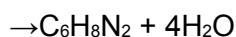
1

Equation must use molecular formulae



12[H] and 4H₂O without correct molecular formula scores 1 out of 2

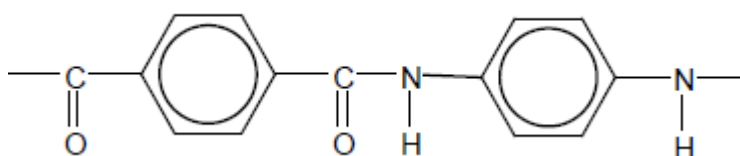
1



Allow + 6H₂ if H₂ / Ni used

Allow -CONH- or -COHN- or -C₆H₄-

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



1

In benzene 120°

1

In cyclohexane $109^\circ 28'$ or $109\frac{1}{2}^\circ$

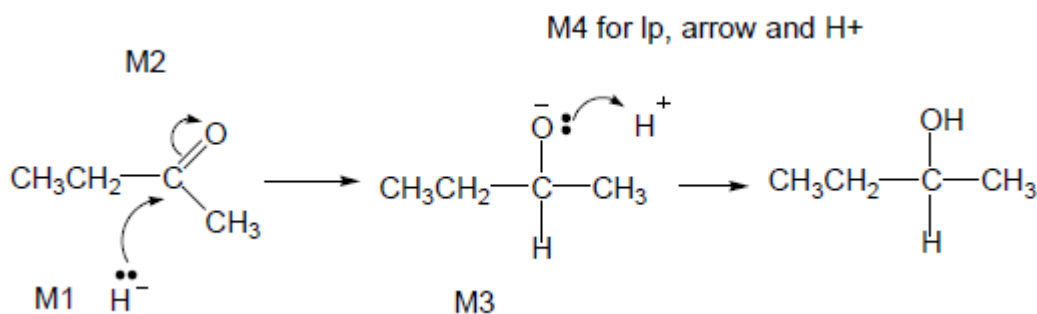
Allow $108^\circ - 110^\circ$

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 $\delta+$ 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 H 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 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 ΔH° hydrogenation of C_6H_6 is $3(-120)$

$$= -360 \text{ kJ mol}^{-1}$$

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

1

M3 Actual ΔH° 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 HNO₃

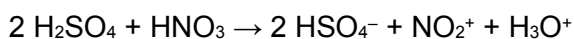
If either or both conc missing, allow one;

1

Conc H₂SO₄

this one mark can be gained in equation

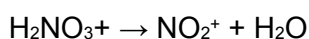
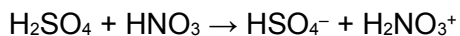
1



OR

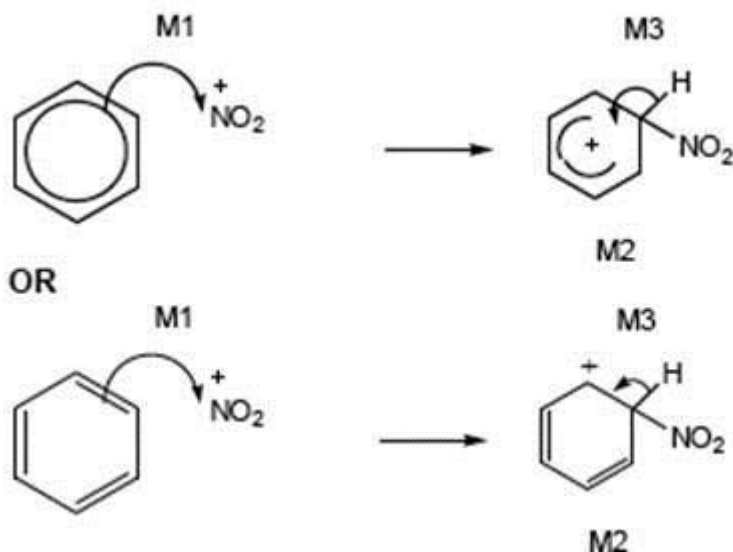


OR via two equations



Allow + anywhere on NO₂⁺

1

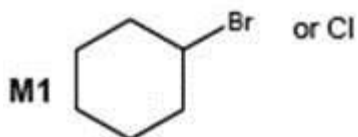


M1 arrow from within hexagon to N or + on N

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)



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}

∴ (expect triene to evolve) 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 / more (stated) stable (1)
Not award if mentions energy required for bond breaking

due to delocalisation (1) or explained

4

(b) (i) phenylamine weaker (1)

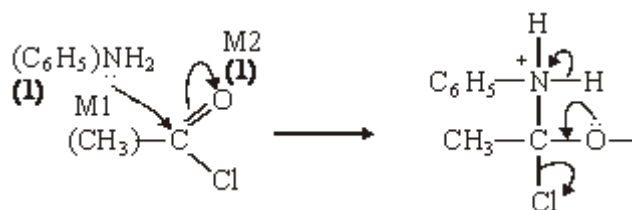
if wrong no marks

lone pair on N (less available) (1)

delocalised into ring (1) or “explained”

3

(ii) addition – elimination (1)



structure (1) M3

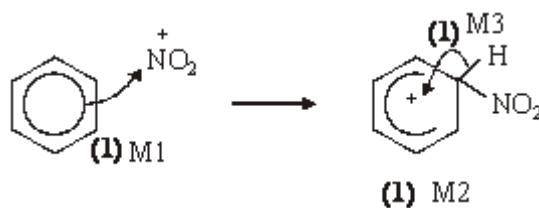
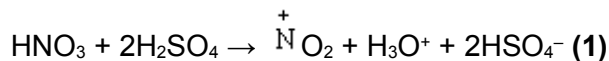
3 arrows (1) M4

N-phenyl ethanamide (1)

6

(iii) conc HNO_3 (1)

conc H_2SO_4 (1)



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 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 $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$
 ignore side chain in mechanism even if wrong
 arrow for M1 must come from inside 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]

Examiner reports

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 kJ mol^{-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.

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.