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A' Level Chemistry

Year 2

Unit 15: Aromatic Chemistry

Summer Examination Revision Pack

The questions in this pack should be attempted **AFTER** completing all other revision.

Grade Accelerator

Recall Definitions
Drawing Diagrams
Using Equations
Drawing Graphs

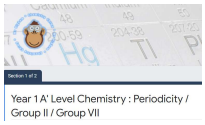
Quizlet

Quizlet Classes

Flashcard Based
Games
Tests & Quizzes
Keyword Spell Checker

Condensed Notes

Keywords & Definitions
Key Concepts
Application
Key Skills



Online Forms

Take Time to Answer
Use Paper & Calculator
Work It Out
Review Missed Marks

Use the 3 Wave Process when completing these revision packs.

1. Complete the questions without assistance
(Can't answer a question? Leave it and move on)
2. Use your notes to fill any gaps after step 1
3. Use the mark scheme to fill in any remaining gaps.

1. Having gaps after step 1 is normal, that's why we are doing revision!
2. If your notes don't help during step 2, they are not good enough!
(Change your note taking method and try to understand the problem)
3. If you don't understand why the mark scheme answer is correct, **see Andy.**

If you struggle with the questions in the pack, **STOP!** and complete some more revision.

If you come to a complete dead-end, **STOP!** and speak to **Andy** asap.

0 8 This question is about nitrobenzenes.

0 8 . 1 Nitrobenzene reacts when heated with a mixture of concentrated nitric acid and concentrated sulfuric acid to form a mixture of three isomeric dinitrobenzenes.

Write an equation for the reaction of concentrated nitric acid with concentrated sulfuric acid to form the species that reacts with nitrobenzene.

[1 mark]

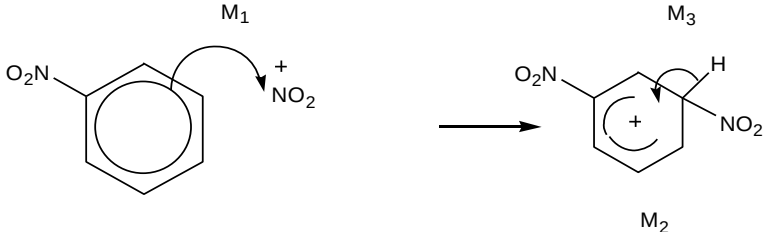
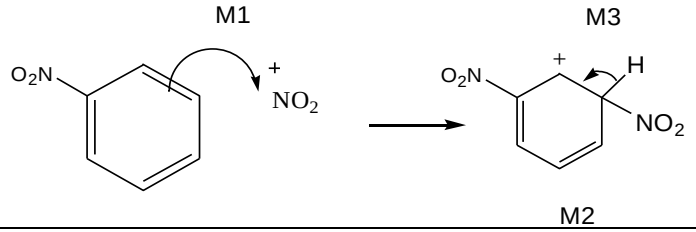
0 8 . 2 Name and outline a mechanism for the reaction of this species with nitrobenzene to form 1,3-dinitrobenzene.

[4 marks]

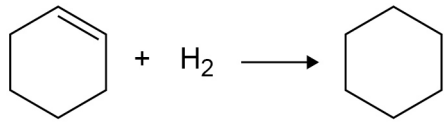
Name of mechanism _____

Mechanism

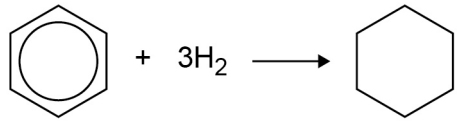
Turn over for the next question

Question	Answers	Mark	Additional Comments/Guidance
08.1	$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$	1	Allow $H_2SO_4 + HNO_3 \rightarrow NO_2^+ + HSO_4^- + H_2O$ Allow a combination of equations which produce NO_2^+ Penalise equations which produce SO_4^{2-}
08.2	Electrophilic substitution.  OR Kekule  	1 3	Ignore nitration M1 Arrow from inside hexagon to N or + on N (Allow NO_2^+) M2 Structure of intermediate • horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6) M3 Arrow from bond into hexagon (Unless Kekule) • Allow M3 arrow independent of M2 structure • + on H in intermediate loses M2 not M3

0 6 Data about the hydrogenation of cyclohexene and of benzene are given.



$\Delta H^{\ominus} = -120 \text{ kJ mol}^{-1}$



$\Delta H^{\ominus} = -208 \text{ kJ mol}^{-1}$

0 6 . 1 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.

[6 marks]

0 6 . 2 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 marks]

9

0 7 Acyl chlorides are useful reagents in synthesis. They react with aromatic compounds and also with alcohols.

0 7 . 1 CH_3CH_2COCl reacts with benzene in the presence of $AlCl_3$ in an electrophilic substitution reaction.

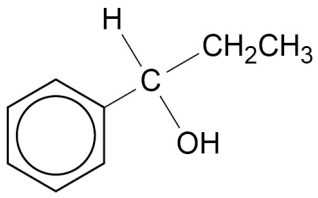
Give an equation for the reaction of CH_3CH_2COCl with $AlCl_3$ to form the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

[4 marks]

Equation _____

Mechanism

0 7 . 2 The organic product in Question **07.1** can be converted into the alcohol shown.



Give the IUPAC name of the alcohol.
Give the reagent needed for this reaction and name the mechanism.

[3 marks]

IUPAC name _____

Reagent _____

Name of mechanism _____

0 7 . 3 The alcohol shown in Question **07.2** reacts with ethanoyl chloride to form an ester.

Describe what would be observed when the alcohol reacts with ethanoyl chloride.
Name the mechanism for the reaction to form the ester.
Draw the structure of the ester.

[3 marks]

Observation _____

_____

Name of mechanism _____

Structure of ester

10

Turn over for the next question

<table>
<tr><th>Question</th><th colspan="2">Answers</th><th>Additional Comments/Guidance</th><th>Mark</th></tr>
<tr><td rowspan="5">06.1</td><td colspan="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.</td><td rowspan="5">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^{o} bond angle
2c) C–C bonds equal in length / C–C bond lengths between single and double bond

Stage 3 Stability
3a) Expected $\Delta H^{\ominus}$ hydrog^{n} of cyclohexatriene = –360 kJ mol^{-1}
3b) $\Delta H^{\ominus}$ hydrog^{n} benzene (is less exothermic) by 152 kJ mol^{-1}
3c) Benzene lower in energy than cyclohexatriene / Benzene is more stable</td><td rowspan="5">6</td></tr>
<tr><td>Level 3

5-6 marks</td><td>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.</td></tr>
<tr><td>Level 2

3-4 marks</td><td>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.

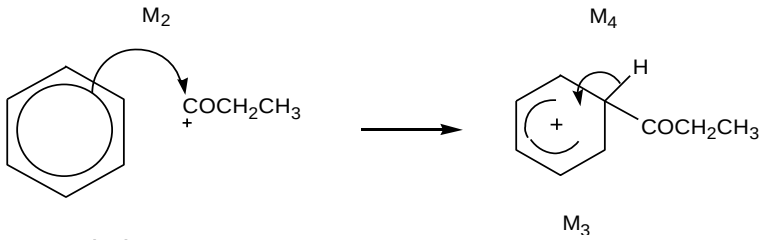
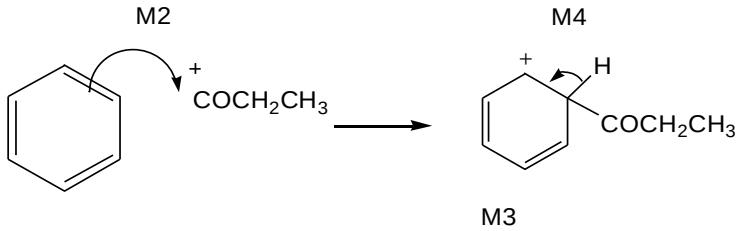
Answer is mainly coherent and shows a progression through the stages. Some steps in each stage may be incomplete.

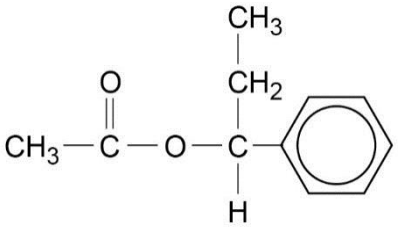
Some errors in use of sign and language in Stage 3.</td></tr>
<tr><td>Level 1

1-2 marks</td><td>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.</td></tr>
<tr><td>Level 0
0 marks</td><td>Insufficient correct chemistry to gain a mark.</td></tr>
</table>

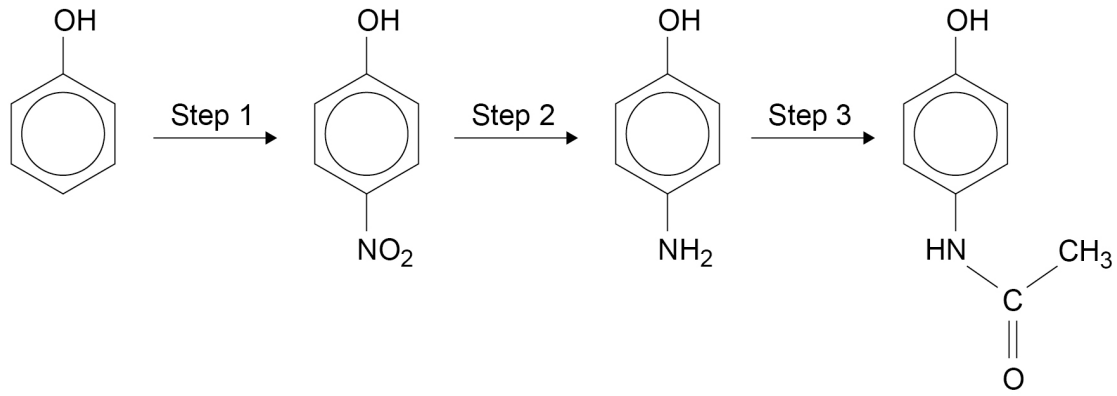
06.2	Value within range –239 to –121 Double bonds separated by one single bond / alternating (or shown in structure) Allows some delocalisation/overlap of p orbitals	1 1 1	If outside range including positive values CE=0 The wording ' close enough to allow delocalisation' would score M2 and M3 Ignore reference to hydration here
Total		9	

07.1	$AlCl_3 + CH_3CH_2COCl \longrightarrow CH_3CH_2-\overset{+}{C}{=}O + AlCl_4^-$		**M**1	Allow + on C or O in equation – But must be on C in mechanism
	 OR Kekule 			M2 Arrow from inside hexagon to C or + on C M3 Structure of intermediate • horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6) M4 Arrow from bond into hexagon (Unless Kekule) • Can allow M4 arrow independent of wrong M3 structure • + on H in intermediate loses M3 not M4 • Ignore Cl^- and $AlCl_4^-$ used in M4
07.2	1-phenylpropan-1-ol $NaBH_4$ / $LiAlH_4$ Nucleophilic addition	1-phenylpropan-1-ol H_2 with Ni/Pd/Pt Addition/hydrogenation	1 1 1	Both numbers needed for name Ignore solvents

07.3	Misty fumes / steamy fumes (Nucleophilic) addition-elimination 	1 1 1	Allow sweet/fruity smell / white fumes Not smoke
Total		10	

Do not write outside the box

0 8 Paracetamol is a medicine commonly used to relieve mild pain.
Traditionally, paracetamol has been made industrially in a three-step synthesis from phenol.



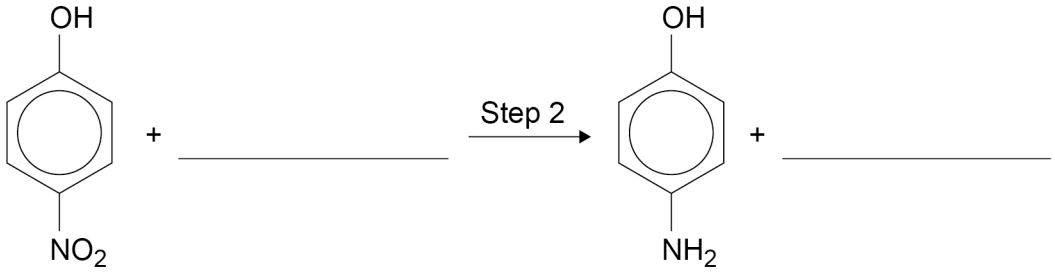
phenol 4-nitrophenol 4-aminophenol paracetamol

0 8 . 1 Name the mechanism of the reaction in Step **1**.

[1 mark]

0 8 . 2 Complete the equation for the reaction in Step **2**.

[1 mark]

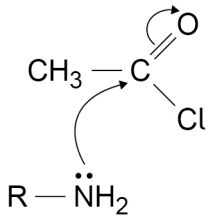


Do not write outside the box

0 8 . 3 In theory, either ethanoyl chloride or ethanoic anhydride could be used in Step **3**.

Complete the mechanism for the reaction of 4-aminophenol with ethanoyl chloride. RNH_2 is used to represent 4-aminophenol in this mechanism.

[2 marks]



0 8 . 4 In practice, ethanoic anhydride is used in the industrial synthesis rather than ethanoyl chloride.

Give **one** reason why ethanoyl chloride is **not** used in the industrial synthesis.

[1 mark]

Question 8 continues on the next page

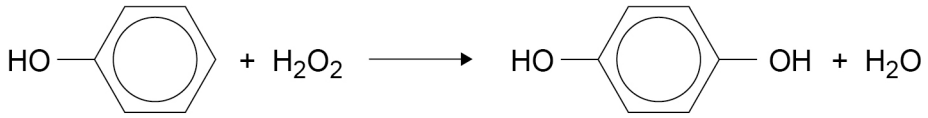
Do not write outside the box

0 8 . 5 In Step **3** other aromatic products are formed as well as paracetamol.

Draw the structure of **one** of these other aromatic products.

[1 mark]

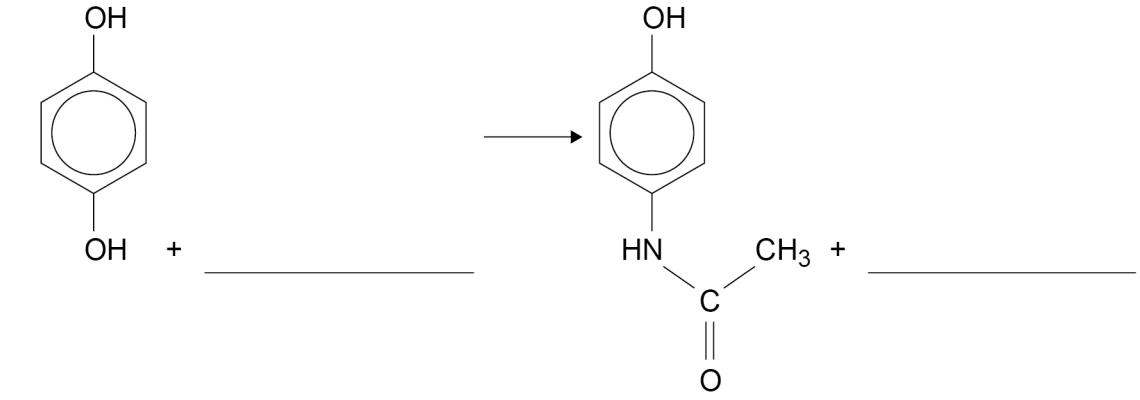
0 8 . 6 Chemists have recently developed a two-step process to produce paracetamol from phenol.
In the first step, phenol is oxidised to hydroquinone.



hydroquinone

In the second step, hydroquinone reacts with ammonium ethanoate to form paracetamol.

Complete the equation for this second step.



hydroquinone paracetamol

[1 mark]

Do not write outside the box

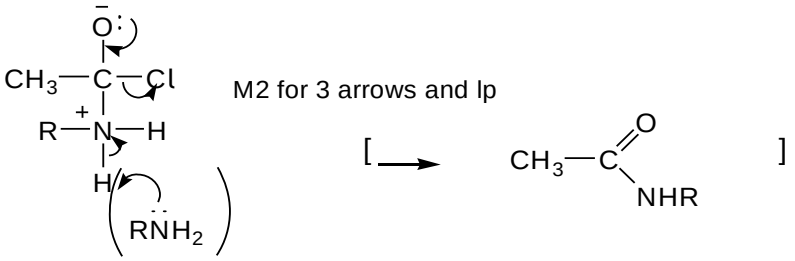
0 8 . 7 Calculate the mass, in kg, of hydroquinone (M_r = 110.0) needed to produce 250 kg of paracetamol.

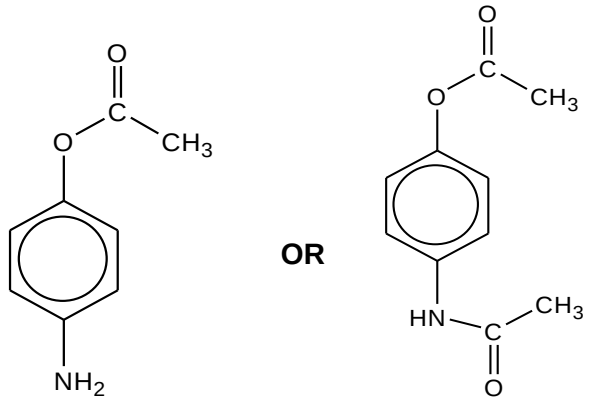
[3 marks]

Mass _____ kg

10

Turn over for the next question

Question	Answers	Additional Comments/Guidelines	Mark
G 08.1	Electrophilic substitution both words needed	Allow minor spelling errors e.g. electrophillic or subsitution Ignore nitration	1
08.2	+ $3H_2$ …… + $2H_2O$	Allow 6[H]	1
08.3	 M2 for 3 arrows and lp M1 for structure	M1 for structure of ion including 2 charges (+ on N must be correct in both cases if drawn twice) M2 for 3 arrows and lp on O - may be scored in two steps Ignore use of RNH_2 to remove H^+ in M2, but penalise use of Cl^-	2
08.4	Corrosive **OR** forms strong acid/HCl (fumes) **OR** vulnerable to hydrolysis **OR** dangerous (to use)	Allow anhydride is less corrosive **OR** does not form strong acid fumes **OR** less vulnerable to hydrolysis **OR** ethanoyl chloride is more expensive Allow reacts violently / extremely exothermic / extremely vigorous Ignore toxic / harmful / hazardous	1

08.5	 **OR**		1
08.6	+ CH_3COONH_4 ..... + $2H_2O$	Allow CH_3COO^- / $CH_3CO_2^-$ and NH_4^+ Allow NH_4CH_3COO	1
08.7	*Via moles* M1 M_r paracetamol = 151(.0) M2 Amount paracetamol = 250×10^3 / 151.0 = 1655.6 mol **OR** (250×10^3) / M1 (= amount hydroquinone used) M3 Mass hydroquinone = 1655.6 × 110.0 = 182119 g = 182 kg **OR** correct answer to M2 × 110.0 / 1000	*OR via mass* M1 M_r paracetamol = 151(.0) So 110 g hydroquinone forms 151 g paracetamol M2 Mass hydroquinone needed 250 × 110 / 151.0 **OR** 250 × 110 / M1 = 182 kg Min 2sf If Mr values used wrong way round can score M2	M1 M2 M3

Do not write outside the box

0 4 Aspirin can be produced by reacting salicylic acid with ethanoic anhydride.
An incomplete method to determine the yield of aspirin is shown.

1. Add about 6 g of salicylic acid to a weighing boat.

2. Place the weighing boat on a 2 decimal place balance and record the mass.

3. Tip the salicylic acid into a 100 cm^3 conical flask.

4. _____

5. Add 10 cm^3 of ethanoic anhydride to the conical flask and swirl.

6. Add 5 drops of concentrated phosphoric acid.

7. Warm the flask for 20 minutes.

8. Add ice-cold water to the reaction mixture and place the flask in an ice bath.

9. Filter off the crude aspirin from the mixture and leave it to dry.

10. Weigh the crude aspirin and calculate the yield.

0 4 . 1 Describe the instruction that is missing from step **4** of the method.

Justify why this step is necessary.

[2 marks]

Instruction _____

Justification _____

_____

_____

0 4 . 2 Suggest a suitable piece of apparatus to measure out the ethanoic anhydride in step **5**.

[1 mark]

_____

0 4 . 3 Identify a hazard of using concentrated phosphoric acid in step **6**.

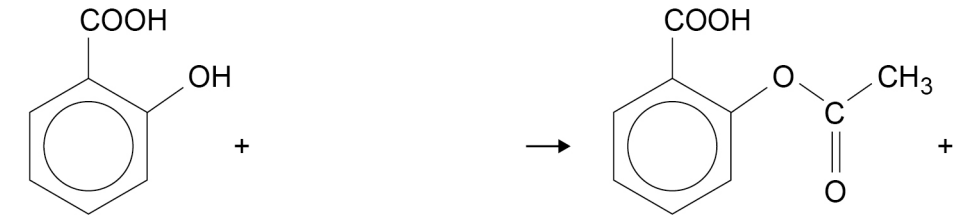
[1 mark]

_____

Do not write outside the box

0 4 . 4 Complete the equation for the reaction of salicylic acid with ethanoic anhydride to produce aspirin.

[1 mark]



Salicylic acid Aspirin

0 4 . 5 A 6.01 g sample of salicylic acid (M_r = 138.0) is reacted with 10.5 cm^3 of ethanoic anhydride (M_r = 102.0).
In the reaction the yield of aspirin is 84.1%

The density of ethanoic anhydride is 1.08 g cm^{-3}

Show by calculation which reagent is in excess.

Calculate the mass, in g, of aspirin (M_r = 180.0) produced.

[5 marks]

Reagent in excess _____

Mass of aspirin _____ g

Turn over ►

Do not write outside the box

0 4 . 6 Suggest **two** ways in which the melting point of the crude aspirin collected in step **9** would differ from the melting point of pure aspirin.

[2 marks]

Difference 1 _____

_____

Difference 2 _____

_____

0 4 . 7 The crude aspirin can be purified by recrystallisation using hot ethanol (boiling point = 78 °C) as the solvent.

Describe **two** important precautions when heating the mixture of ethanol and crude aspirin.

[2 marks]

Precaution 1 _____

_____

Precaution 2 _____

_____

0 4 . 8 The pure aspirin is filtered under reduced pressure.
A small amount of cold ethanol is then poured through the Buchner funnel.

Explain the purpose of adding a small amount of cold ethanol.

[1 mark]

_____

_____

_____

0 4 . 9 A sample of the crude aspirin is kept to compare with the purified aspirin.

Describe **one** difference in appearance you would expect to see between these two solid samples.

[1 mark]

_____

_____

_____

16

Question	Answers	Additional comments/Guidelines	Mark
04.1	**M1** (Re)weigh the empty boat **M2** In order to calculate the (exact) mass of salicylic acid added to the reaction mixture		1 1
04.2	10 cm^3 measuring cylinder (if volume given – allow between 10 to 50 cm^3) Or a 10 cm^3 pipette Or burette / graduated pipette Or 10 cm^3 syringe		1
04.3	Corrosive	Allow skin burn / permanent eye damage Ignore irritant / toxic	1
04.4	LHS + $(CH_3CO)_2O$ RHS + CH_3COOH		1
04.5	**M1** Amount salicylic acid = $^{6.01}/_{138}$ = 4.36×10^{-2} mol **M2** Mass $(CH_3CO)_2O$ = 10.5 × 1.08 = 11.34 g **M3** Amount $(CH_3CO)_2O$ = $^{11.34}/_{102}$ = 1.11×10^{-1} mol **M4** $(CH_3CO)_2O$ is in excess **M5** Mass aspirin = M1 × 0.841 × 180 = 6.59 g	Allow conseq from wrong mole ratio in 04.4 Must show and state that ethanoic anhydride is in excess For M4/M5 ecf from M1/M3 Allow 2 sf or more.	1 1 1 1 1 1

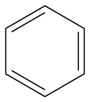
04.6	**M1** Value lower		1
	M2 Range of values	For M2 allow mpt not sharp or a larger range of melting points	1

04.7	**M1** (Ethanol is flammable so) use a water bath to heat / do not use a Bunsen burner	Must give practical step, not just state hazard	1
	M2 Heat to temp below bp (so ethanol does not boil away)	Allow use min vol solvent	1

04.8	To remove any soluble impurities	Allow To avoid aspirin dissolving (small amount cold solvent used) Allow To remove/(wash away) any ethanolic solution on the product.	1

04.9	Pure product will have (larger) crystals / needle-like crystals / lighter in colour	Allow whiter, less grey, more crystalline, less powdery, shinier, single colour Must be tied to pure product Allow opposite points tied to the crude product	1

Do not write outside the box

0 4 Kekulé suggested this structure for benzene. 

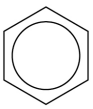
Benzene is now represented by this structure. 

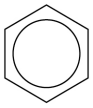
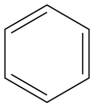
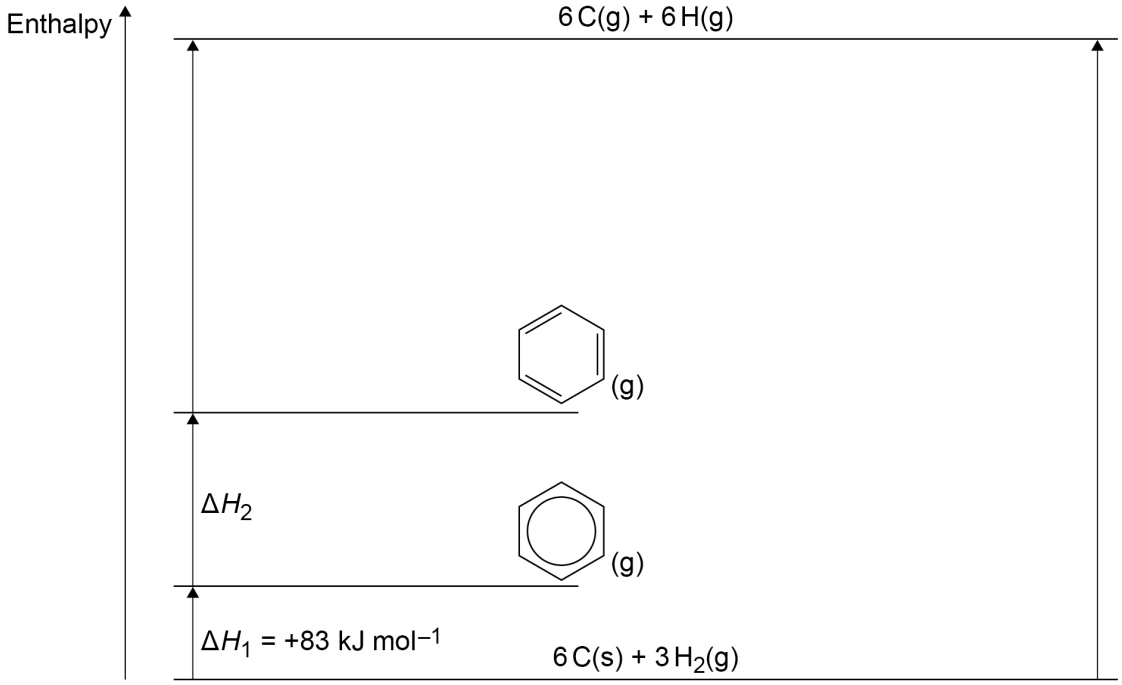
Figure 3 shows the relative stability of  compared to  .

Figure 3



Do not write outside the box

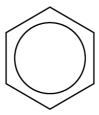
0 4 . 1 Use **Figure 3** and the data shown in **Table 1** to calculate ΔH_2

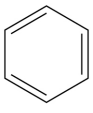
[3 marks]

Table 1

	ΔH / kJ mol^{-1}
Enthalpy of atomisation for carbon	+715
Enthalpy of atomisation for hydrogen	+218
Bond enthalpy (C–C)	+348
Bond enthalpy (C=C)	+612
Bond enthalpy (C–H)	+412

ΔH_2 _____ kJ mol^{-1}

0 4 . 2 Explain, in terms of structure and bonding, why 

is more thermodynamically stable than 

[1 mark]

_____

_____

_____

Turn over ►

Do not write outside the box

0 4 . 3 A mixture of concentrated nitric acid and concentrated sulfuric acid reacts with benzene.

Figure 4 shows the incomplete mechanism for this reaction.

Name the mechanism.

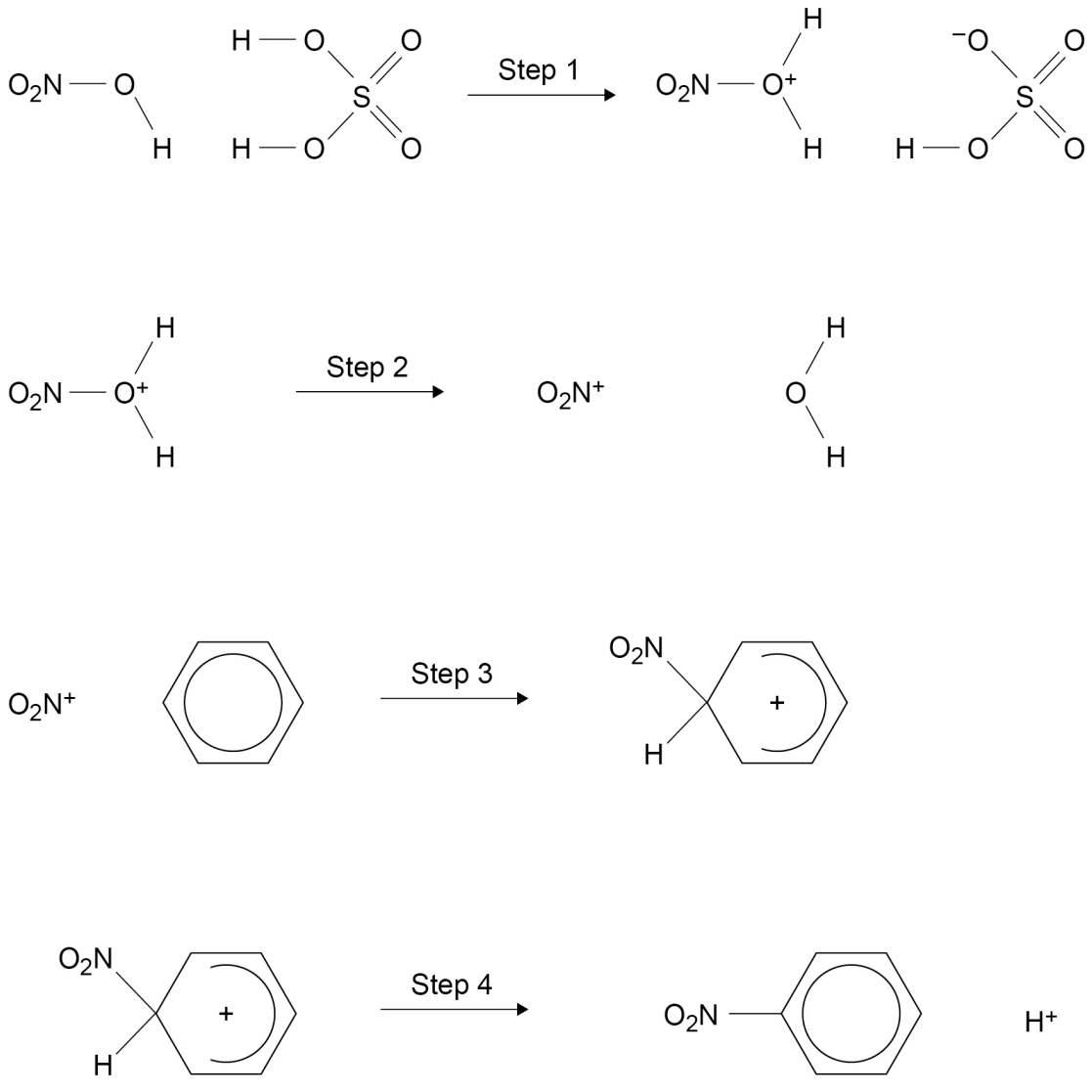
Complete the mechanism in **Figure 4** by adding

- any lone pairs of electrons involved in each step
- **two** curly arrows in step **1**
- a curly arrow in step **2**
- a curly arrow in step **3**
- a curly arrow in step **4**.

[5 marks]

Name of mechanism _____

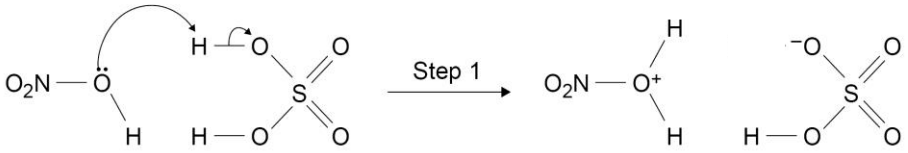
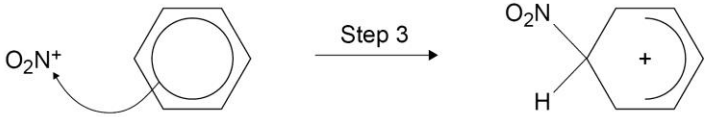
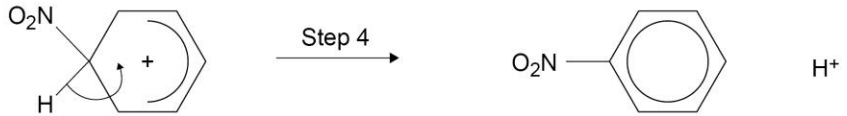
Figure 4



9

Question	Answers	Additional Comments/Guidelines	Mark
04.1	(3 x 612) + (3 x 348) + (6 x 412) = 5352 (6 x 715) + (6 x 218) = 5598 ΔH_2 = M2 - M1 - 83 = +163 kJ mol^{-1}	For LHS For RHS	M1 M2 M3

Question	Answers	Additional Comments/Guidelines	Mark
04.2	(π) electrons delocalised		1

Question	Answers	Additional Comments/Guidelines	Mark
04.3	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

Do not write outside the box

0 8 Benzene reacts with methanoyl chloride (HCOCl) in the presence of a catalyst.

0 8 . 1 Give an equation for the overall reaction when benzene reacts with methanoyl chloride.

Name the organic product.

[2 marks]

Equation _____

Name _____

0 8 . 2 Identify the catalyst needed in this reaction.

Give an equation to show how the catalyst is used to form the electrophile, $[HCO]^+$

[2 marks]

Catalyst _____

Equation _____

0 8 . 3 Outline the mechanism for the reaction of benzene with the electrophile, $[HCO]^+$

[3 marks]

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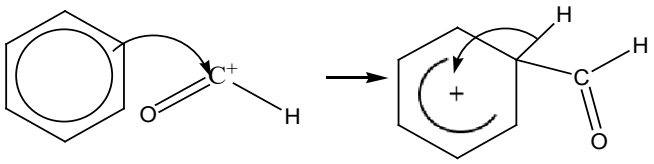
Question	Answers	Additional Comments/Guidelines	Mark
08.1	$C_6H_6 + HCOCl \rightarrow C_6H_5CHO + HCl$ Or shown as structural formulae Benzaldehyde	 Allow phenyl methanal Allow Benzenealdehyde or Benzene carbaldehyde If ethanoyl chloride used allow ecf for name : phenyl ethanone	1 1 (2 x AO2)

Question	Answers	Additional Comments/Guidelines	Mark
08.2	$AlCl_3$ $HCOCl + AlCl_3 \rightarrow [HCO]^+ + [AlCl_4]^-$	Allow Aluminium chloride Allow Iron (III) chloride / bromide or formulae Allow + on C or O in equation Can score M1 in equation	1 1 (1 x AO1, 1 x AO2)

Question	Answers	Additional Comments/Guidelines	Mark
08.3		M1 Arrow from inside hexagon to C or + on C M2 Structure of intermediate • horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6) M3 Arrow from bond into hexagon (Unless Kekule) • Can allow M3 arrow independent of wrong M2 structure • + on H in intermediate loses M2 not M3 • Ignore Cl^- and $AlCl_4^-$ used in M3	M1 M2 M3 (3 x AO2)