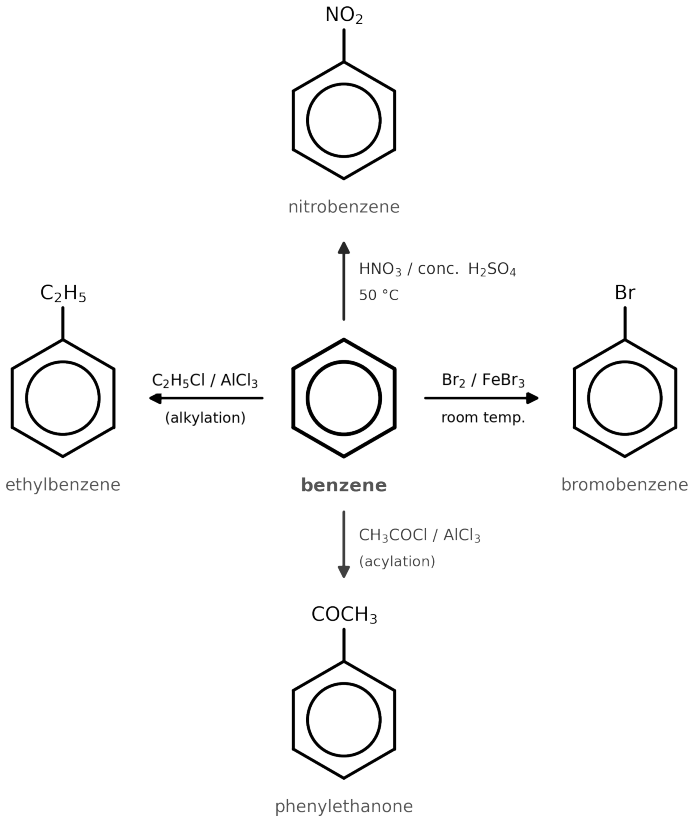
Aromatic Chemistry

Scaffolded Worksheets — Student Booklet (greyscale print version)

OCR A Level Chemistry A (H432) · Module 6.1.1 Aromatic compounds



Contents

How each worksheet works

CORE — the questions for the lesson. When the slide says "NOW → Worksheet", this is where you go. They are the textbook summary questions for that section plus questions of the same kind: no gap-fills, you have to think.

HARDER — the same skills with more to think about. For when you have finished the core questions; they are meant to take time.

EXAM-STYLE — one question in exam wording, also done in class: in one go, in silence, then marked against the mark scheme.

Worksheet 8 is the whole set of chapter practice questions from the textbook (pages 451–453), to be done after the topic.

University-level work is NOT in this booklet: it is on the separate Uni worksheet, and beyond that in the Stretch Pack.

Self-check — tick the "I can" statements at the end of each worksheet.

Greyscale print version — section headings are told apart by their rule: CORE single, HARDER double, EXAM-STYLE dashed. Boxes with a dashed outline are for you to fill in.

Name: _____

Worksheet 1

Meet benzene: Kekulé vs delocalised

OCR A Level Chemistry A (H432) · Specification 6.1.1 (a) (b) · core questions about 20 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(a) the comparison of the Kekulé model of benzene with the subsequent delocalised models for benzene in terms of p-orbital overlap forming a delocalised π-system

(b) the experimental evidence for a delocalised, rather than Kekulé, model for benzene in terms of bond lengths, enthalpy change of hydrogenation and resistance to reaction

Examiner guidance: You may represent benzene in equations and mechanisms as the Kekulé structure OR as a hexagon with a circle. HSW1,7: development of the model for benzene over time. HSW11: acceptance of the delocalised model by the scientific community in the light of supporting experimental evidence.

Name: _____ Class: _____ Date: _____

CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

1. State the empirical formula of benzene. **[1 mark]**

2. Draw the Kekulé structure of benzene and the delocalised structure of benzene. State one difference in what the two models predict about the C–C bond lengths. **[3 marks]**

Kekulé structure	**Delocalised structure**

3. Explain how X-ray diffraction helped scientists to develop the delocalised model of benzene. **[3 marks]**

4. The enthalpy change of hydrogenation of cyclohexene is −120 kJ mol^{-1}. **[4 marks]**

(a) Predict the enthalpy change of hydrogenation of the Kekulé structure of benzene (cyclohexa-1,3,5-triene). Show your working.

(b) The actual enthalpy change of hydrogenation of benzene is −208 kJ mol^{-1}. Calculate the difference between the two values and explain what it tells you about benzene.

5. Explain why the delocalised model of benzene accounts for the observed stability of benzene better than the Kekulé model. **[3 marks]**

6. Cyclohexene decolourises bromine water at room temperature; benzene does not. Explain why this observation was a problem for Kekulé's model. **[2 marks]**

HARDER Harder

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. The enthalpy change of hydrogenation of cyclohexa-1,3-diene (two C=C bonds next to each other) is −232 kJ mol^{-1}. **[3 marks]**

(a) Predict the value using the cyclohexene data in question 4.

(b) Calculate the difference and suggest why the diene is slightly more stable than predicted.

H2. A student says that every C–C bond in benzene is 'one-and-a-half bonds'. Explain what the student means and how the bond-length data (C–C 0.153 nm, C=C 0.134 nm, benzene 0.139 nm) support the idea. **[2 marks]**

H3. Kekulé's model was also criticised on these grounds: it predicts TWO different isomers of 1,2-dibromobenzene (the two Br atoms on a C=C, or on a C–C), but only ONE has ever been found. Explain how the delocalised model resolves this. **[2 marks]**

H4. X-ray diffraction finds carbon atoms easily but hydrogen atoms only with great difficulty. Suggest why. **[1 mark]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. In 1865 Kekulé proposed a model for benzene with alternating single and double bonds. Describe and explain TWO pieces of experimental evidence that led scientists to replace this model with a delocalised model. In your answer, refer to bond lengths and to enthalpy changes. **[6 marks]**

Self-check — I can…

- ☐ draw both models of benzene
- ☐ explain the bond-length evidence
- ☐ use hydrogenation data to calculate the 152 kJ mol^{-1} stabilisation

Worksheet 2

Naming aromatic compounds

OCR A Level Chemistry A (H432) · Specification 6.1.1 (c) · core questions about 20 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(c) use of IUPAC rules of nomenclature for systematically naming substituted aromatic compounds

Examiner guidance: Use locant numbers to identify positions of substitution, e.g. 2,4-dinitromethylbenzene. HSW8: introduction of systematic nomenclature.

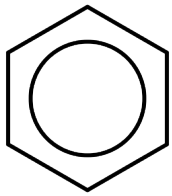
Name: _____ Class: _____ Date: _____

CORE Core questions

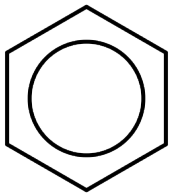
Do these in the lesson when the slide says NOW → Worksheet.

1. Draw the structures of the following aromatic compounds. **[5 marks]**

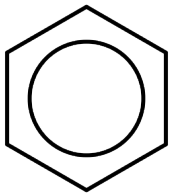
a 1,2,4-tribromobenzene



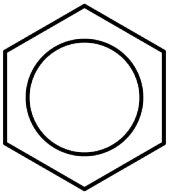
b 1,3-dinitrobenzene



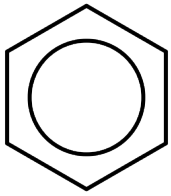
c 2,4,6-trichloromethylbenzene



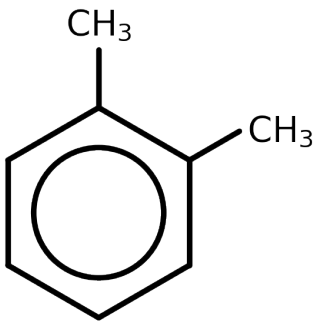
d phenylpropanone



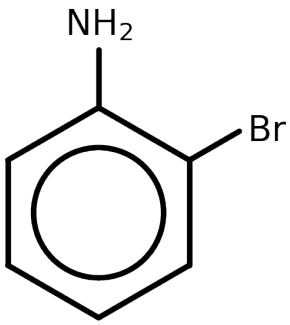
e 2,3-dichlorobenzoic acid



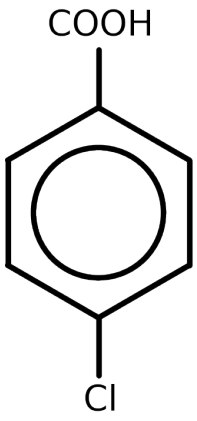
2. Name the following molecules. **[3 marks]**



a

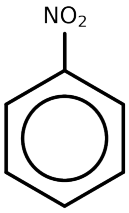


b

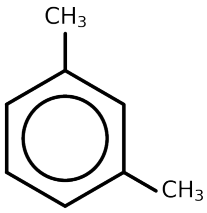


c

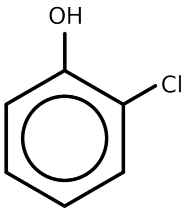
3. Name compounds A–H. **[8 marks]**



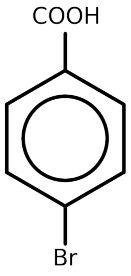
A



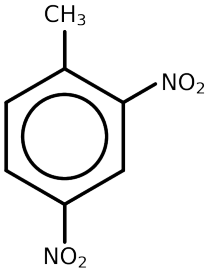
B



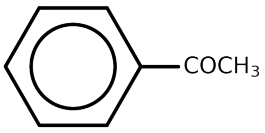
C



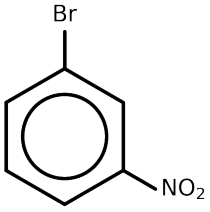
D



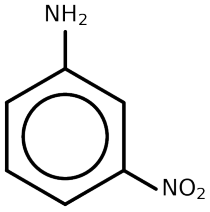
E



F



G



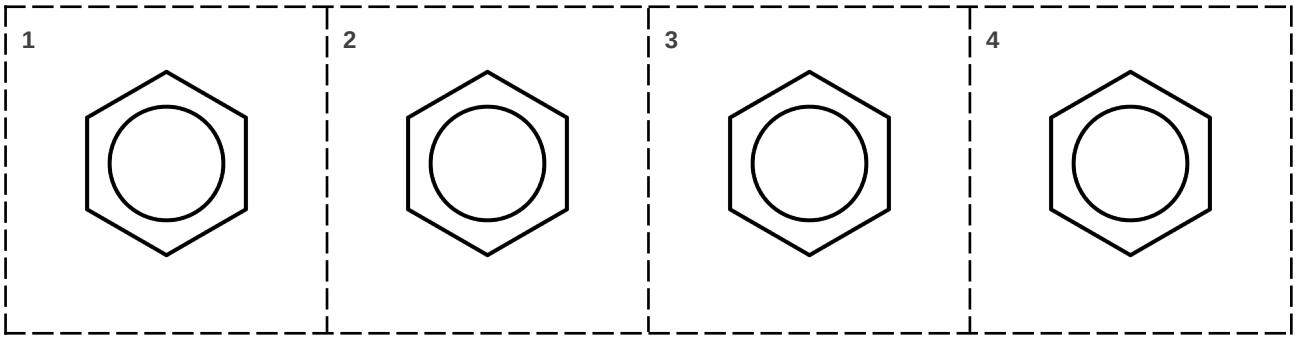
H

	Name		Name
A		E	
B		F	
C		G	
D		H	

4. Each of these names is WRONG. Write the correct name and say what the mistake is. **[5 marks]**
(a) 4-nitro-1-methylbenzene (b) 3-chloro-5-bromophenol (c) 2,4,6-trinitrotoluene (d) 1,5-dichlorobenzene (e) hydroxybenzene

5. Compound X has the molecular formula C_7H_7Cl and contains a benzene ring. Draw and name all FOUR possible structures. **[4 marks]**

1 2 3 4

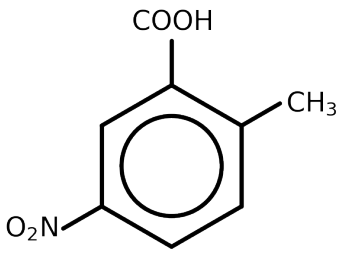


6. Give the molecular formula of: (a) methylbenzene (b) phenol (c) nitrobenzene (d) benzoic acid (e) phenylamine. **[5 marks]**

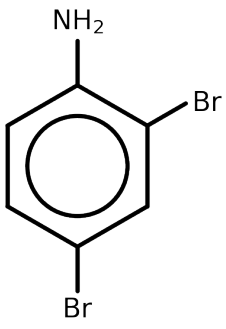
HARDER Harder

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

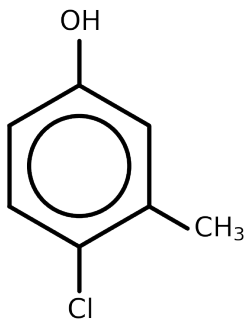
H1. Name compounds P, Q and R. Each has THREE groups on the ring — use alphabetical order and the lowest locants. **[3 marks]**



P

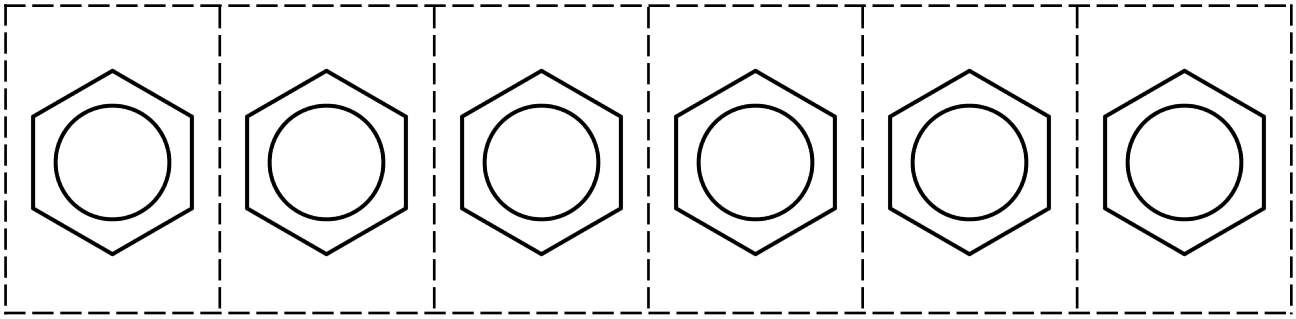


Q

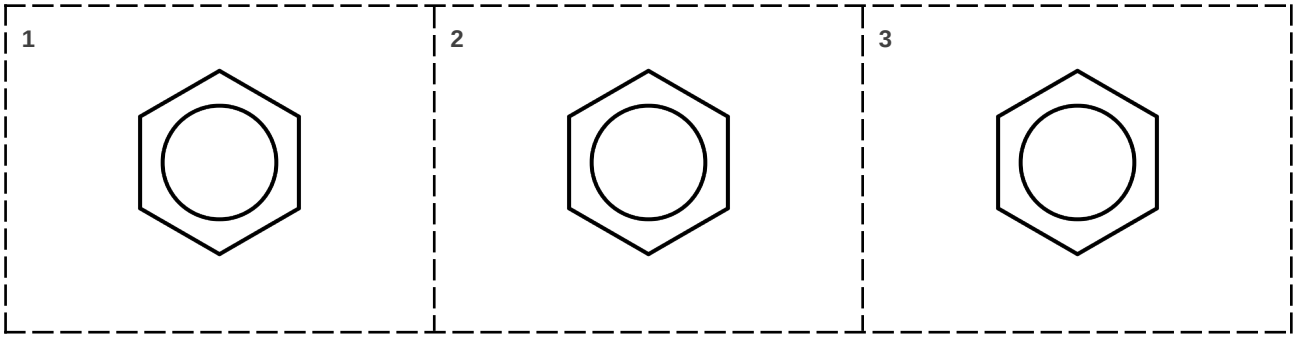


R

H2. There are SIX structural isomers of dinitromethylbenzene, $CH_3C_6H_3(NO_2)_2$. Draw and name all six. **[6 marks]**



H3. A compound has the molecular formula C_8H_8O. It contains a benzene ring and a C=O group. Draw and name THREE possible structures. **[3 marks]**



EXAM-STYLE **Exam-style question**

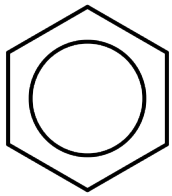
Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

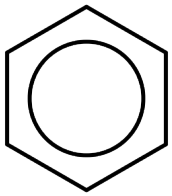
E1. Compound Y has the molecular formula $C_6H_4Cl_2$ and contains a benzene ring. **[5 marks]**

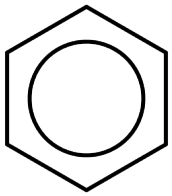
(a) Draw and name all the possible structural isomers of Y.

(b) In one of these isomers all four hydrogen atoms are in identical environments. Identify this isomer and explain your answer.

(a)







Self-check — I can…

- ☐ draw a structure from a name
- ☐ name a ring with one, two or three groups
- ☐ spot a wrong name and fix it

Worksheet 3

Electrophilic substitution: nitration

OCR A Level Chemistry A (H432) · Specification 6.1.1 (d)(i) (e) · core questions about 25 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(d(i)) the electrophilic substitution of aromatic compounds with concentrated nitric acid in the presence of concentrated sulfuric acid

(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation

Examiner guidance: For the nitration mechanism you should include the equation for the formation of NO_2^+. For the halogenation mechanism the electrophile can be assumed to be X^+. HSW1,2,8: using reaction mechanisms to explain organic reactions.

Name: _____ Class: _____ Date: _____

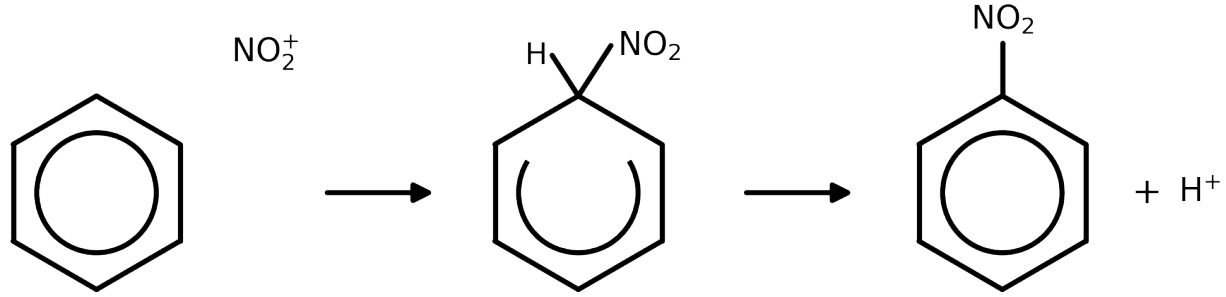
CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

1. Benzene reacts by electrophilic substitution. Define the terms (a) electrophile (b) substitution. **[2 marks]**

2. Write the equation for the formation of the electrophile in the nitration of benzene, and name the electrophile. **[2 marks]**

3. Complete the mechanism for the nitration of benzene: add the two curly arrows and the positive charge on the intermediate. **[3 marks]**



benzene intermediate

Where the marks are — exactly. Learn these three lines; they are what the examiner checks.

Mark	The examiner must see
1 · Curly arrow from the delocalised ring to N of NO_2^+	Tail ON the circle — that is where the electron pair is — next to the carbon being attacked. Head touching the N atom of NO_2^+ — the atom that carries the + (never an O). An arrow that starts on the hexagon edge (a σ bond), ends on the wrong atom, or points the other way scores nothing.
2 · The intermediate, drawn exactly	Open the circle into a HORSESHOE that stops at the two carbons either side of the carbon holding the H and the NO_2 — it must not reach that carbon. Write + INSIDE the horseshoe (the charge is spread over the other five carbons; never on the carbon with the H, never on the H itself). Draw H AND NO_2 on the SAME carbon.
3 · Curly arrow from the C–H bond into the ring, and H^+ leaves	Tail on the MIDDLE of the C–H bond (a bond is breaking — never on the H atom). Head pointing into the ring, towards the +, to re-form the circle. Products: nitrobenzene + H^+.
Making the electrophile	$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
Regenerating the catalyst (H_2SO_4)	$H^+ + HSO_4^- \rightarrow H_2SO_4$

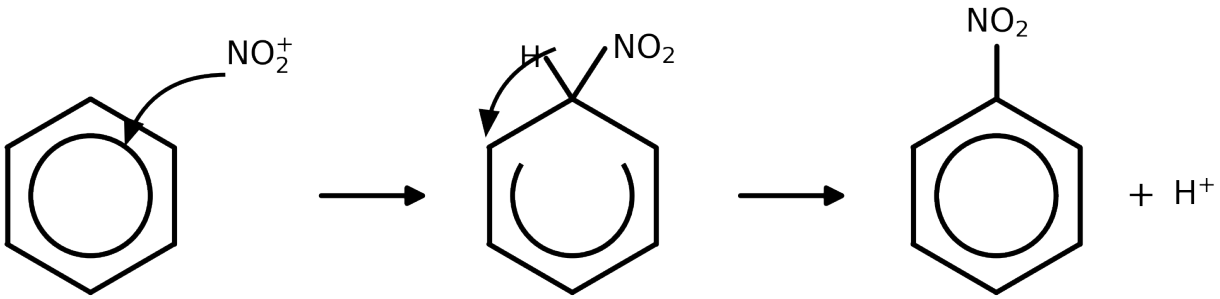
4. Now mark your own mechanism. Tick every line you can see on YOUR drawing.

Mark point	✓
Equation for making the electrophile (e.g. $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$)	
Arrow 1: tail ON the circle, head TOUCHING the electrophilic atom (N of NO_2^+ / Br^+ / C of CH_3CO^+)	
Intermediate: horseshoe stops either side of the carbon holding H and the new group; + INSIDE the horseshoe	
Intermediate: H AND the new group drawn on the SAME carbon	
Arrow 2: tail on the MIDDLE of the C–H bond, head INTO the ring towards the +	
Products: substituted benzene + H^+ ; catalyst regenerated ($H^+ + HSO_4^- \rightarrow H_2SO_4$ or $H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$)	

5. Write the equation that regenerates the catalyst, and use it to explain why sulfuric acid is described as a catalyst. **[2 marks]**

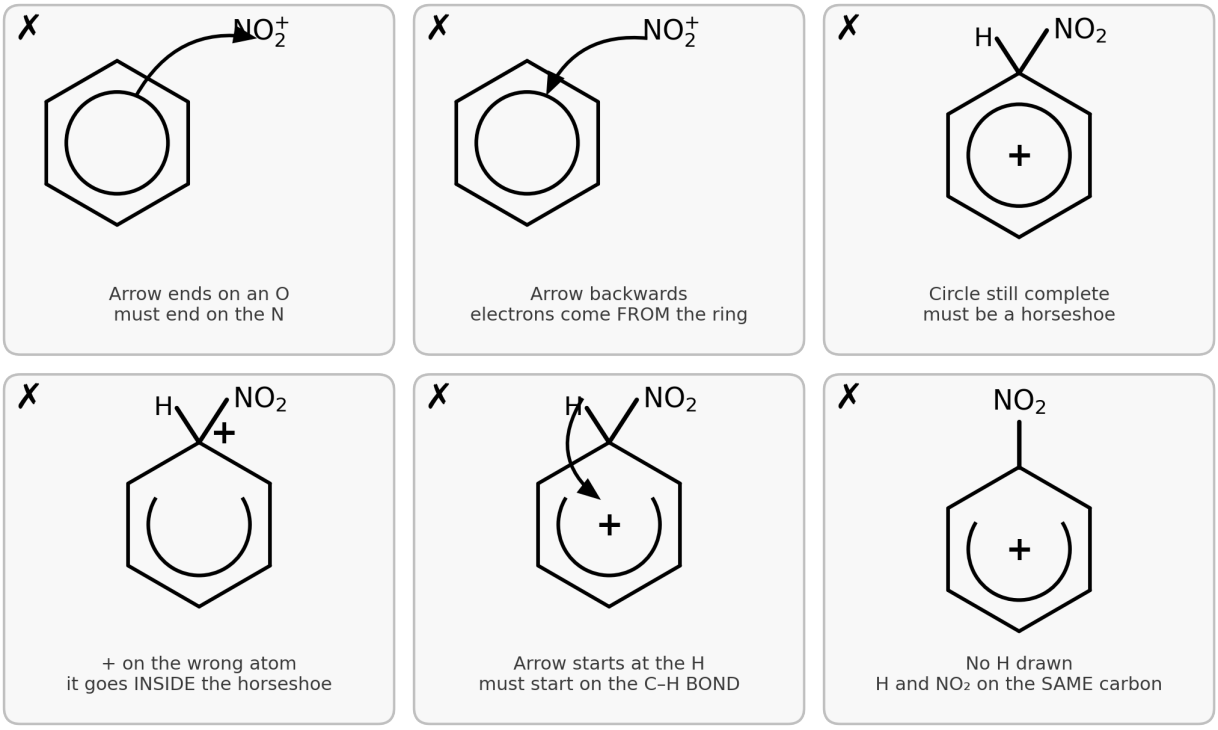
6. State the conditions for the mono-nitration of benzene and explain what happens if the mixture is heated more strongly. **[2 marks]**

7. A student's mechanism is shown below. It contains THREE mistakes. Describe each mistake and how to correct it. **[3 marks]**



benzene intermediate

8. Six more mechanisms, each losing exactly ONE mark. Under each drawing write which mark (1, 2 or 3) is lost and how to fix it. **[6 marks]**



HARDER Harder

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. Methylbenzene is nitrated with concentrated nitric and sulfuric acids to form 4-nitromethylbenzene. Draw the mechanism, using NO_2^+ as the electrophile. (The NO_2 goes to the carbon opposite the CH_3.) **[4 marks]**

Draw the mechanism here (use the whole width)

H2. In a preparation, 15.6 g of benzene gave 19.7 g of nitrobenzene. Calculate the percentage yield. (Mr: benzene 78.0, nitrobenzene 123.0) **[3 marks]**

H3. In the same preparation the temperature is kept below 55 °C, and the crude product is washed with sodium carbonate solution before it is purified. Explain both precautions. **[2 marks]**

H4. Concentrated nitric acid on its own nitrates benzene only very slowly. Explain why, using the equation in question 2. **[2 marks]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. Phenylethanone, $C_6H_5COCH_3$, reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid to form 3-nitrophenylethanone. Outline the mechanism for this reaction. Your answer should include the formation of the electrophile and should show how sulfuric acid behaves as a catalyst. **[6 marks]**

Draw the mechanism here (use the whole width)

Self-check — I can…

- ☐ write the equation for forming NO_2^+
- ☐ draw the nitration mechanism and say where each mark is
- ☐ explain how H_2SO_4 acts as a catalyst

Worksheet 4

Halogenation and halogen carriers

OCR A Level Chemistry A (H432) · Specification 6.1.1 (d)(ii) (e) (f) · core questions about 25 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(d(ii)) the electrophilic substitution of aromatic compounds with a halogen in the presence of a halogen carrier

(e) the mechanism of electrophilic substitution in arenes for nitration and halogenation

(f) the explanation of the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π-system in benzene compared with the localised electron density of the π-bond in alkenes

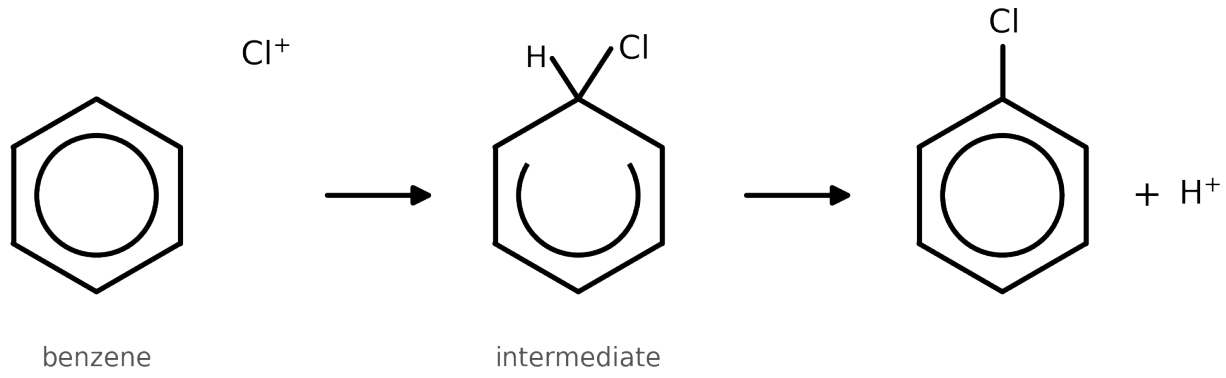
Examiner guidance: Halogen carriers include iron, iron halides and aluminium halides. For the nitration mechanism you should include the equation for the formation of NO_2^+. For the halogenation mechanism the electrophile can be assumed to be X^+. HSW1,2,8: using reaction mechanisms to explain organic reactions. HSW2,5: use the delocalised benzene model to explain reactivity.

Name: _____ Class: _____ Date: _____

CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

1. Benzene reacts with chlorine by an electrophilic substitution mechanism. Outline this mechanism on the skeleton below, including an equation to show how the electrophile is generated from Cl_2 and $AlCl_3$. **[4 marks]**



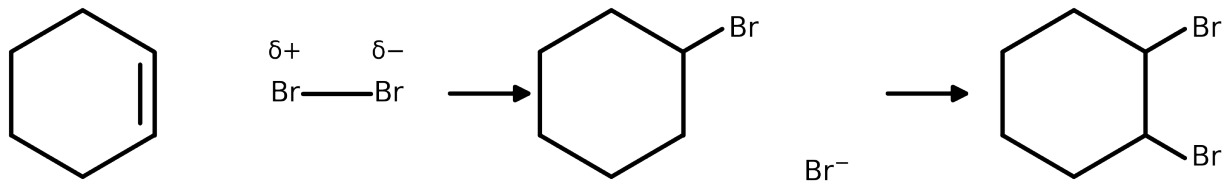
2. Write THREE equations for the bromination of benzene using bromine and iron(III) bromide: (a) formation of the electrophile (b) the overall reaction (c) regeneration of the catalyst. **[3 marks]**

3. Explain the role of the halogen carrier in the bromination of benzene. **[2 marks]**

4. State what you would observe when bromine is added to (a) cyclohexene (b) benzene (c) benzene with iron filings. **[3 marks]**

5. Explain why benzene is much less reactive towards bromine than an alkene such as cyclohexene. **[4 marks]**

6. Complete the mechanism for the electrophilic ADDITION of bromine to cyclohexene: add the curly arrows, the + charge on the intermediate and the lone pair on Br^-. **[3 marks]**



cyclohexene intermediate 1,2-dibromocyclohexane

HARDER Harder

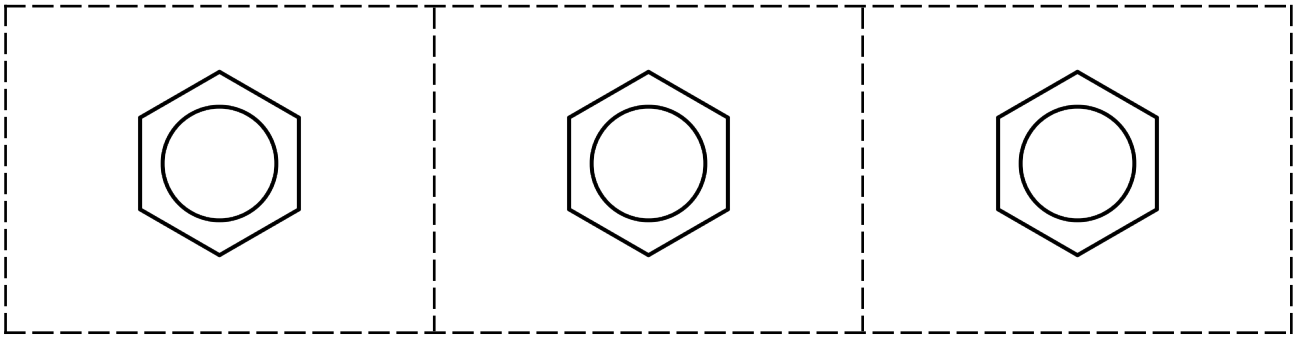
Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. Some textbooks draw the electrophile in bromination as a polarised Br–Br molecule bonded to $FeBr_3$ (Br–Br···$FeBr_3$) instead of Br^+. Draw the first step of the mechanism in this form, showing the dipole and BOTH curly arrows. **[3 marks]**

Draw here

H2. $AlCl_3$ and $FeBr_3$ can act as halogen carriers, but NaCl cannot. Suggest why. **[2 marks]**

H3. Chlorobenzene reacts with more chlorine, with $AlCl_3$, to give a mixture of dichlorobenzenes. Draw and name the three possible isomers, and suggest why a mixture is formed. **[4 marks]**



H4. Iodine does not react with benzene even in the presence of a halogen carrier. Suggest a reason. **[1 mark]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. Bromobenzene is manufactured from benzene and bromine using iron filings. **[6 marks]**

(a) Explain how iron filings act as a catalyst in this reaction even though the halogen carrier is iron(III) bromide.

(b) Outline the mechanism for the formation of bromobenzene from benzene.

(c) State one hazard of the reaction and how it is controlled.

(b) mechanism

Self-check — I can…

- ☐ draw the halogenation mechanism with the electrophile-forming equation
- ☐ explain what a halogen carrier does
- ☐ give the 4-mark explanation of why benzene resists bromination

Worksheet 5

Friedel–Crafts: alkylation and acylation

OCR A Level Chemistry A (H432) · Specification 6.1.1 (d)(iii) (g) · core questions about 25 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(d(iii)) the electrophilic substitution of aromatic compounds with a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring

(g) the interpretation of unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms

Examiner guidance: See also 6.2.4(d) — carbon–carbon bond formation in synthesis. Extra information may be provided on exam papers.

Name: _____ Class: _____ Date: _____

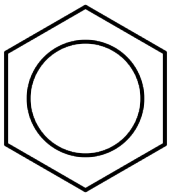
CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

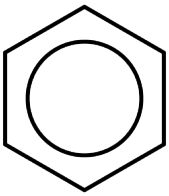
1. Benzene reacts with 2-chloropropane, in the presence of an $AlCl_3$ catalyst, by electrophilic substitution. Construct the equation for this reaction, using structural formulae. **[2 marks]**

2. Deduce the structure of the organic product expected from the reaction of each of the following compounds with benzene in the presence of $AlCl_3$: (i) $(CH_3)_2CHCOCl$ (ii) C_6H_5COCl. **[2 marks]**

(i)



(ii)



3. Use curly arrows to show the mechanism for the reaction between $(CH_3)_2CHCOCl$ and benzene, clearly showing the role of the catalyst. **[4 marks]**

Draw the mechanism here (use the whole width)

4. Explain why Friedel–Crafts reactions are important in organic synthesis. **[1 mark]**

5. Write equations for the formation of the electrophile from (a) chloroethane (b) ethanoyl chloride, each with $AlCl_3$, and (c) the regeneration of the catalyst at the end of the reaction. **[3 marks]**

6. Complete the table for reactions of benzene with $AlCl_3$ as the catalyst. **[4 marks]**

Reagent	Electrophile	Name of organic product
CH_3Cl		
CH_3CH_2Cl		
CH_3COCl		
C_6H_5COCl		

HARDER Harder

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. Industrially, (1-methylethyl)benzene (cumene) is made by reacting benzene with propene using phosphoric acid, H_3PO_4, as the catalyst. Suggest the identity of the electrophile and how it forms, then draw the mechanism. **[4 marks]**

Draw the mechanism here (use the whole width)

H2. Benzene reacts with 1-chloropropane and $AlCl_3$ to give mainly (1-methylethyl)benzene rather than propylbenzene. Suggest why. (Think back to carbocation stability in 4.1.3.) **[2 marks]**

H3. Draw the organic product formed when excess benzene reacts with $ClCO–CH_2CH_2–COCl$ in the presence of $AlCl_3$. **[1 mark]**

Product

H4. In an acylation, more than one mole of $AlCl_3$ is needed for each mole of acyl chloride, whereas in an alkylation a small amount is enough. Suggest why. **[1 mark]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. Phenylethanone, $C_6H_5COCH_3$, can be made by reacting benzene with ethanoyl chloride in the presence of aluminium chloride. **[6 marks]**

(a) Write an equation to show the formation of the electrophile.

(b) Outline the mechanism for the reaction of this electrophile with benzene.

(c) Write an equation to show how the catalyst is regenerated.

(d) Name the type of reaction.

(b) mechanism

Self-check — I can…

- ☐ write equations for alkylation and acylation
- ☐ draw the acylation mechanism, arrow to the C=O carbon
- ☐ predict the product of an unfamiliar electrophile

Worksheet 6

Phenol: a weak acid with an activated ring

OCR A Level Chemistry A (H432) · Specification 6.1.1 (h) (i) (j) · core questions about 25 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(h) the weak acidity of phenols shown by the neutralisation reaction with NaOH but absence of reaction with carbonates

(i) the electrophilic substitution reactions of phenol: (i) with bromine to form 2,4,6-tribromophenol, (ii) with dilute nitric acid to form a mixture of 2-nitrophenol and 4-nitrophenol

(j) the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the π-system from an oxygen p-orbital in phenol

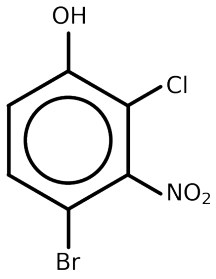
Examiner guidance: PAG7 (qualitative analysis); see also 6.3.1(c). Note that nitration of phenol does NOT require concentrated HNO_3 or the presence of a concentrated H_2SO_4 catalyst. Illustrated by the reactions with bromine and with nitric acid. The explanation is ONLY in terms of the susceptibility of the ring to attack — NOT the stability of the intermediate. HSW2,5.

Name: _____ Class: _____ Date: _____

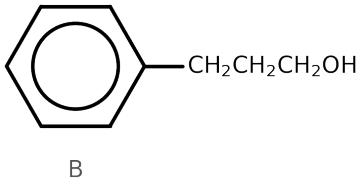
CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

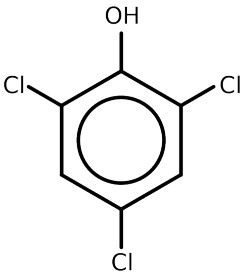
1. (a) Name each of the molecules A–D. (b) Identify the molecules that are phenols. **[5 marks]**



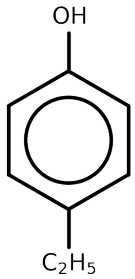
A



B



C



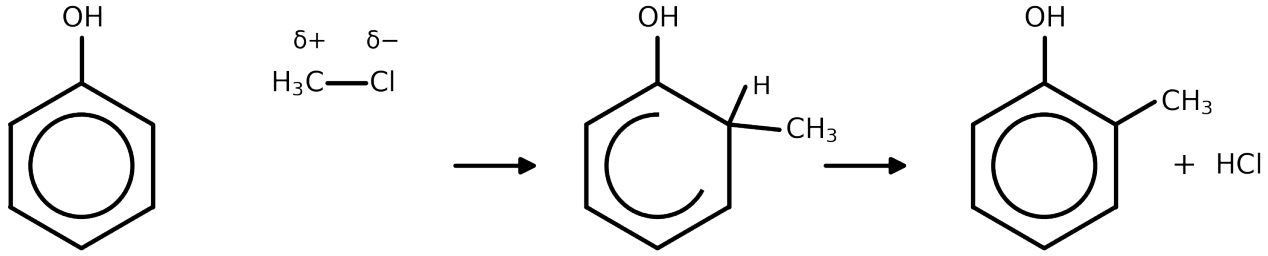
D

2. Write an equation to show the reaction of 2-hydroxyphenol (benzene-1,2-diol) with an EXCESS of sodium hydroxide. **[1 mark]**

3. Outline how you would carry out a test to distinguish between solutions of pent-1-ene and phenol. **[1 mark]**

4. Explain why bromine reacts more readily with phenol than with benzene. **[3 marks]**

5. Phenol reacts with chloromethane to form 2-methylphenol. The reactivity of phenol means that a halogen carrier is not required. Complete the mechanism on the skeleton below. (Hint: the ring attacks the electron-deficient carbon atom of chloromethane.) **[4 marks]**



2-methylphenol

6. Write equations (structural formulae) for the reaction of phenol with (a) sodium hydroxide (b) sodium (c) excess bromine water (d) dilute nitric acid, and state what you would SEE in (c). **[5 marks]**

7. Phenol does not react with sodium carbonate solution, but ethanoic acid does. Explain what this tells you about phenol. **[2 marks]**

HARDER **Harder**

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. Predict the organic product when 4-methylphenol reacts with excess bromine water, and explain your answer. **[3 marks]**

H2. K_a values at 298 K: ethanol 1.0×10^{-16}, phenol 1.3×10^{-10}, ethanoic acid 1.7×10^{-5} mol dm^{-3}. Put the three in order of increasing acid strength and explain the order in terms of the stability of the negative ion formed. **[3 marks]**

H3. 2-Hydroxybenzoic acid (salicylic acid) has a phenol group and a carboxylic acid group. Write equations for its reaction with (a) excess sodium hydroxide and (b) sodium carbonate, and state which group(s) react in each case. **[3 marks]**

H4. 4-Nitrophenol is a much stronger acid than phenol. Suggest why. **[2 marks]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. Compound Z is 4-methylphenol. **[7 marks]**

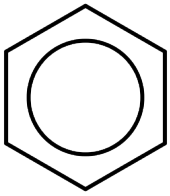
(a) Draw the structure of Z.

(b) Write an equation for the reaction of Z with sodium hydroxide.

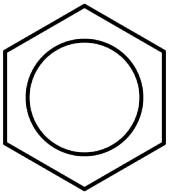
(c) Z reacts with dilute nitric acid to give only ONE mono-nitro product. Draw its structure and explain why only one product forms.

(d) Z reacts with bromine water at room temperature; methylbenzene does not. Explain this difference.

(a) Z



(c) product



Self-check — I can…

- ☐ name phenols and tell them from alcohols
- ☐ write the equations for phenol + NaOH, Na, Br_2 and dilute HNO_3
- ☐ explain why phenol is activated

Worksheet 7

Directing groups and synthesis

OCR A Level Chemistry A (H432) · Specification 6.1.1 (k) (l) · core questions about 25 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(k) the 2- and 4-directing effect of electron-donating groups (OH, NH_2) and the 3-directing effect of electron-withdrawing groups (NO_2) in electrophilic substitution of aromatic compounds

(l) the prediction of substitution products of aromatic compounds by directing effects and the importance to organic synthesis

Examiner guidance: You will NOT be expected to know further electron-donating or electron-withdrawing groups; relevant additional data will be supplied in examinations. HSW5. See also 6.2.5 Organic synthesis.

Name: _____ Class: _____ Date: _____

Data for this worksheet. You must KNOW the first three rows; the rest would be given in an exam.

Group on the ring	Directs the next group to
–OH, –NH_2 (electron-donating, lone pair)	2 and 4
–NO_2 (electron-withdrawing)	3
–R (alkyl, e.g. –CH_3)	2 and 4
–Cl, –Br	2 and 4
–COOH, –COOR, –COR (–$COCH_3$), –CHO	3
–$N^+(CH_3)_3$	3

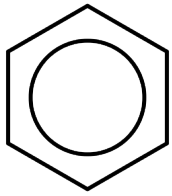
CORE Core questions

Do these in the lesson when the slide says NOW → Worksheet.

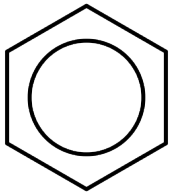
1. Identify each of the following compounds as containing a 2,4-directing or a 3-directing group: (a) $C_6H_5CH_2CH_3$ (b) C_6H_5Cl (c) C_6H_5COOH (d) $C_6H_5N^+(CH_3)_3$. **[4 marks]**

2. Identify and draw the structures of the product(s) of the following reactions: (a) $C_6H_5Br + HNO_3$ (with conc. H_2SO_4) (b) $C_6H_5NO_2 + Br_2 + FeBr_3$ (c) $C_6H_5COOCH_2CH_3 + CH_3Cl + AlCl_3$. **[3 marks]**

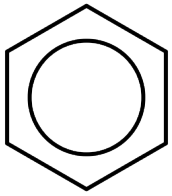
(a)



(b)



(c)

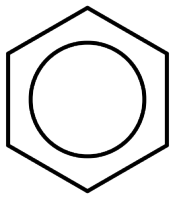


3. Starting from benzene, suggest a two-step synthesis of (a) 3-nitromethylbenzene (b) 2-nitromethylbenzene. Give reagents and conditions and explain the order of the steps. **[4 marks]**

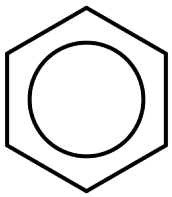
4. Explain, in terms of electron density, why an –OH group directs a second substituent to positions 2 and 4 whereas an $–NO_2$ group directs it to position 3. **[2 marks]**

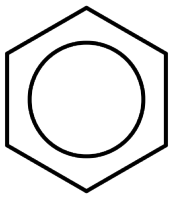
5. Predict the major organic product(s) of (a) phenylethanone + Cl_2 with $AlCl_3$ (b) methylbenzene + chloroethane with $AlCl_3$. Draw and name them. **[3 marks]**

(a)



(b)





HARDER Harder

Same ideas, more to think about. Start these when you have finished the core questions — they are meant to take time.

H1. When a ring already carries TWO groups, the more strongly activating group usually decides where the next one goes. Predict the major product(s) of (a) 4-methylphenol + dilute nitric acid (b) 3-nitromethylbenzene + Br_2/$FeBr_3$. Explain each prediction. **[4 marks]**

H2. Nitro groups can be reduced to amino groups using tin and concentrated hydrochloric acid. Use this to plan a synthesis from benzene of (a) 4-bromophenylamine (b) 3-bromophenylamine. Give reagents and conditions for every step. **[4 marks]**

H3. Methylbenzene is converted to 2,4,6-trinitromethylbenzene (TNT) by prolonged nitration. Write the overall equation and explain why the three nitro groups take up positions 2, 4 and 6. **[3 marks]**

H4. A student plans to make 4-nitrophenylethanone by nitrating phenylethanone. Explain why the plan fails, and why simply reversing the two steps (nitrate, then acylate) does not work either. **[3 marks]**

EXAM-STYLE **Exam-style question**

Exam wording, exam marks. Done in class: in silence, in one go, then marked against the mark scheme.

E1. 1-Bromo-4-nitrobenzene can be made from benzene in two steps. **[8 marks]**

(a) Give the reagents and conditions for each step and explain why the steps must be carried out in this order.

(b) Outline the mechanism for the second step.

(c) Explain why carrying out the steps in the reverse order would give a different product.

(b) mechanism

Self-check — I can…

- ☐ classify a group as 2,4- or 3-directing
- ☐ predict the product of a substitution on a substituted ring
- ☐ plan a two-step synthesis and justify the order

Worksheet 8

Chapter practice questions

OCR A Level Chemistry A (H432) · Specification 6.1.1 (a)–(l) · core questions about 80 min · STUDENT VERSION · greyscale print

Specification 6.1.1 says you must be able to demonstrate and apply knowledge and understanding of:

(a) Kekulé model vs delocalised model: p-orbital overlap → delocalised π-system
(b) evidence for delocalisation: bond lengths, enthalpy change of hydrogenation, resistance to reaction
(c) IUPAC rules for naming substituted aromatic compounds
(d) electrophilic substitution: nitration, halogenation, Friedel–Crafts
(e) the mechanism of electrophilic substitution for nitration and halogenation
(f) why benzene resists bromination compared with alkenes: delocalised vs localised π electron density
(g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms
(h) weak acidity of phenols: reacts with NaOH, no reaction with carbonates
(i) phenol + bromine → 2,4,6-tribromophenol; phenol + dilute nitric acid → 2-nitrophenol and 4-nitrophenol
(j) phenol is more easily substituted than benzene: electron pair donated from an oxygen p-orbital into the π-system
(k) OH and NH_2 (electron-donating) direct to 2- and 4-; NO_2 (electron-withdrawing) directs to 3-
(l) predicting substitution products from directing effects; importance to organic synthesis

Name: _____ Class: _____ Date: _____

The Chapter 25 practice questions (textbook pages 451–453), complete. 72 marks, about 80 minutes. Done in class, in one sitting, in silence, then marked against the mark scheme.

EXAM-STYLE Practice questions

Past-paper questions from OCR F324 — the same style as your H432 papers.

1. Salicylic acid is a naturally occurring carboxylic acid, widely used in organic synthesis. The flowchart shows some of its reactions. **[12 marks]**

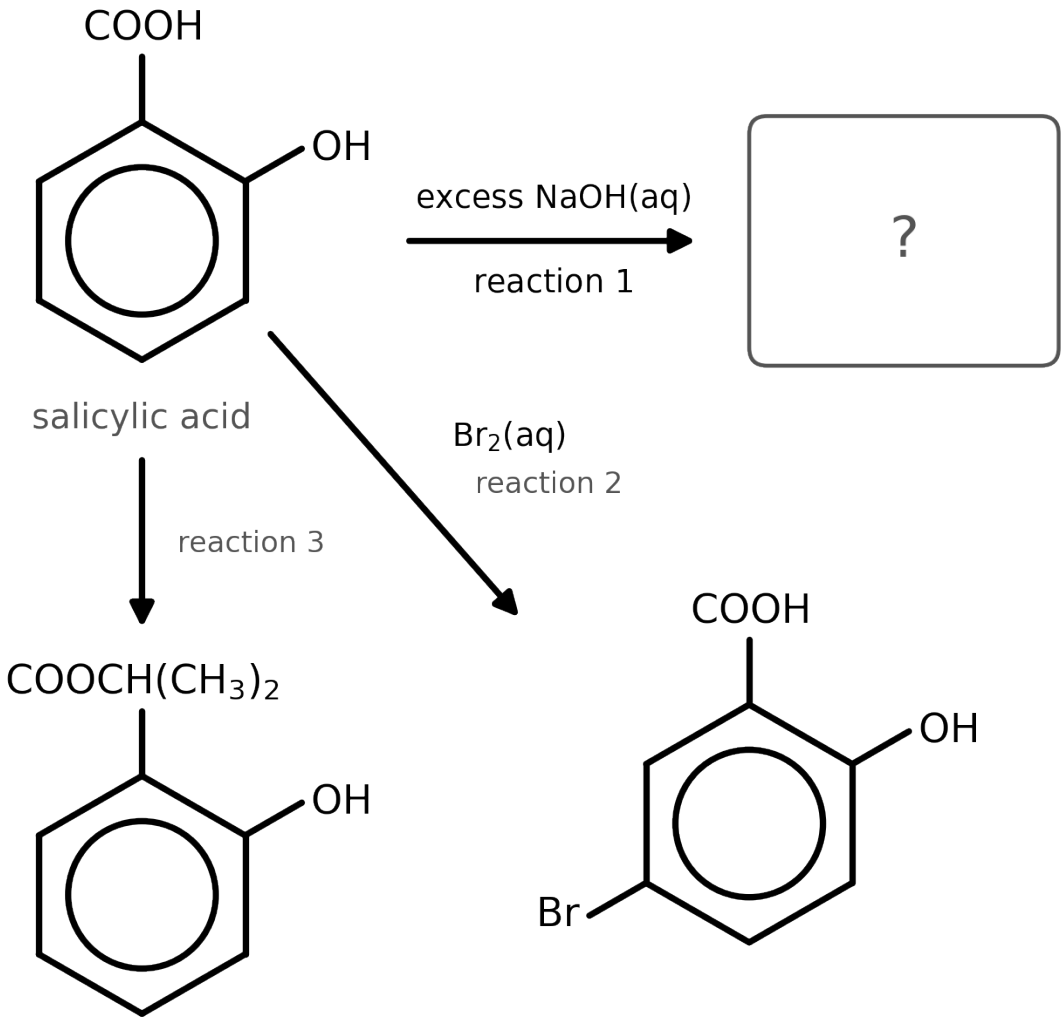
(a)(i) In the box, draw the structure of the organic compound formed by reaction 1.

(ii) Write a chemical equation to represent reaction 2.

(iii) State the reagents and conditions in reaction 3.

(b)(i) Outline the mechanism for the bromination of salicylic acid in reaction 2. A halogen carrier is not required; the electrophile is Br_2.

(ii) Explain why bromine reacts more readily with salicylic acid than with benzene. Use appropriate technical terms, spelled correctly.

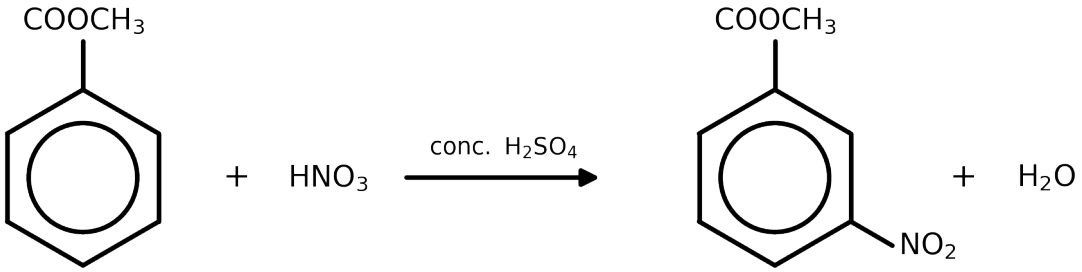

COOH
OH
excess NaOH(aq)
reaction 1
?
salicylic acid
Br_2(aq)
reaction 2
reaction 3
$COOCH(CH_3)_2$
OH
COOH
OH
Br

(b)(i) mechanism

2. In the first stage of the synthesis of a dye, methyl 3-nitrobenzoate is formed. In this stage, methyl benzoate is nitrated by concentrated nitric acid, in the presence of concentrated sulfuric acid as a catalyst. **[6 marks]**

(i) Outline the mechanism for this nitration of methyl benzoate. Show how H_2SO_4 behaves as a catalyst.

(ii) State the name for this type of mechanism.

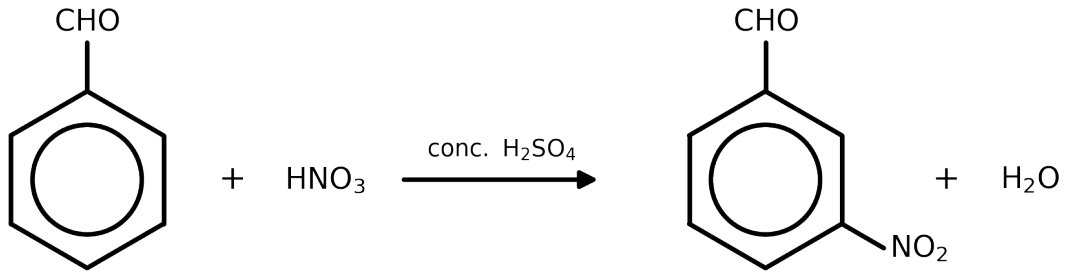


methyl benzoate methyl 3-nitrobenzoate

Draw the mechanism here (use the whole width)

3. Benzaldehyde, C_6H_5CHO, is the simplest aromatic aldehyde and has a characteristic smell of almonds. Benzaldehyde can be nitrated with a mixture of concentrated nitric acid and concentrated sulfuric acid to form 3-nitrobenzaldehyde. **[6 marks]**

Explain, with the aid of curly arrows, the mechanism for the formation of 3-nitrobenzaldehyde. Your answer should clearly show the role of sulfuric acid as a catalyst.



benzaldehyde 3-nitrobenzaldehyde

mechanism

4. Benzene and other arenes can be chlorinated to produce chloroarenes which are used in the manufacture of pesticides, drugs and dyes. **[15 marks]**

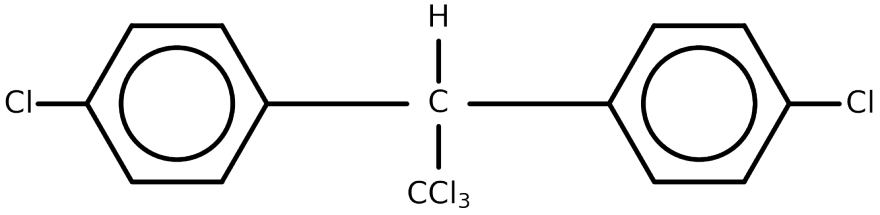
(a) In 1865, Kekulé proposed a model for the structure and bonding of benzene, but there is considerable evidence to suggest that Kekulé's model may not be correct. Scientists have proposed alternative models for the structure and bonding of benzene. Explain the evidence that led scientists to doubt the model proposed by Kekulé.

(b) Chlorobenzene, C_6H_5Cl, is formed by the reaction of benzene and chlorine in the presence of a suitable catalyst, such as $AlCl_3$: $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$. Outline the mechanism for the formation of chlorobenzene from benzene. Show how $AlCl_3$ behaves as a catalyst.

(c) Chlorobenzene reacts with trichloroethanal, Cl_3CCHO, to produce the pesticide DDT (shown below). Construct an equation for the reaction of chlorobenzene with trichloroethanal to form DDT.

(d) Chlorobenzene can be nitrated to form a mixture of products. Suggest why the reaction forms a mixture of products.

(e) Explain why phenol reacts more readily with chlorine than benzene reacts with chlorine. In your answer, you should use appropriate technical terms, spelled correctly.

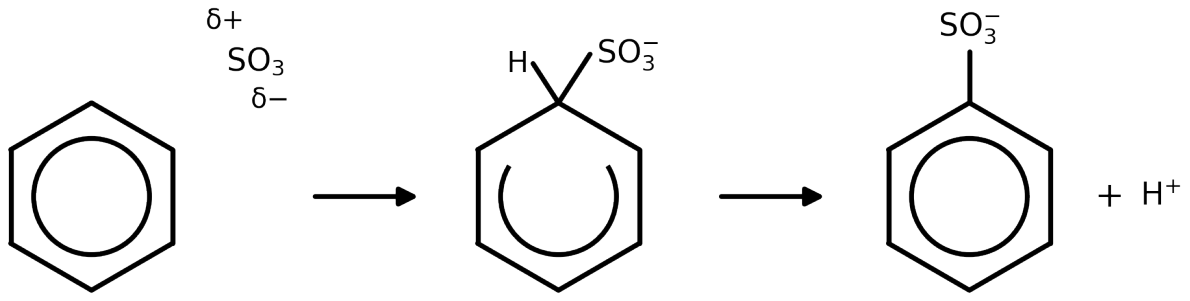


DDT

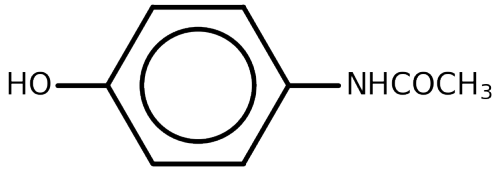
(b) mechanism

5. (a) Benzene can be converted into benzenesulfonic acid, $C_6H_5SO_3H$, which is used in the manufacture of many detergents. The reaction between benzene and sulfur trioxide is an electrophilic substitution reaction. Sulfur trioxide, SO_3, is the electrophile. Part of the mechanism for this reaction is shown below. Complete the mechanism by drawing the intermediate and by adding curly arrows to show the movement of electron pairs in steps 1 and 2. **[6 marks]**

(b) The painkiller paracetamol has the structure shown below. Separate samples of paracetamol are reacted with bromine, Br_2, and with cold sodium hydroxide, NaOH. Draw the structures of possible organic products formed in each reaction.



benzene intermediate



paracetamol

(a) intermediate and arrows — draw on the printed scheme above	**(b) with Br_2**	**(b) with NaOH**

6. The mass spectrum of an aromatic hydrocarbon is found to have a molecular ion peak at m/z value of 106. Elemental analysis showed that the compound had the following composition by mass, C, 90.56% and H, 9.44%. **[8 marks]**

(a) Use the data to find the molecular formula of the aromatic compound.

(b) A student realised that the calculated molecular formula could have a number of different structural isomers. Draw all the possible structural isomers that contain a benzene ring.

(c) In the presence of concentrated nitric acid and concentrated sulfuric acid, one of the isomers, A, reacts to give one mono-nitrated compound, B. Identify A and B.

(b) isomers	**(c) A and B**

7. When monosubstituted aromatic compounds undergo further substitution, the position at which the new substituent attaches to the ring is directed by the original substituent. Use the table to answer the questions which follow. **[8 marks]**

(a)(i) Draw the structure of the major monosubstituted product formed when phenylethanone, $C_6H_5COCH_3$, reacts with chlorine in the presence of $AlCl_3$.

(ii) Show the mechanism for this reaction using curly arrows and illustrating the role of $AlCl_3$ in the reaction.

(b) Identify the two monosubstituted isomers formed when methylbenzene reacts with chloroethane in the presence of $AlCl_3$.

Original substituent	**Position to which new substituent is directed**
–COOH	3
–CH_3 (or any alkyl group)	2, 4
–NO_2	3
–Cl	2, 4
–$COCH_3$	3

(a)(i) product

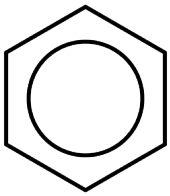
(a)(ii) mechanism (use the whole width)

8. Phenol is much more susceptible to electrophilic attack than benzene. **[5 marks]**

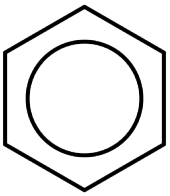
(a) Explain why phenol reacts more readily than benzene with electrophiles.

(b) Phenol reacts with dilute nitric acid to form a mixture of two monosubstituted isomers. Draw the structures of these two isomers and write an equation for the formation of one of these isomers.

(b) 2-isomer



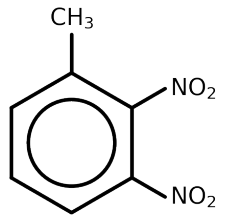
(b) 4-isomer



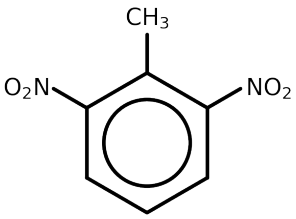
9. Methylbenzene, $C_6H_5CH_3$, is an aromatic hydrocarbon, used widely as a solvent. It is readily nitrated and can form mono-, di-, or tri-nitromethylbenzenes. **[6 marks]**

(a) 4-Nitromethylbenzene can be formed by the nitration of methylbenzene. Outline the mechanism for the formation of 4-nitromethylbenzene from methylbenzene using NO_2^+ as the electrophile.

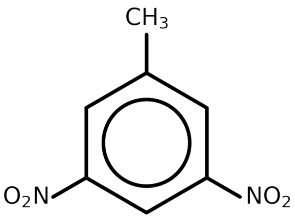
(b) There are six possible structural isomers of $CH_3C_6H_3(NO_2)_2$ that are dinitromethylbenzenes. Four of the isomers are shown below. Draw the structures of the other two isomers.



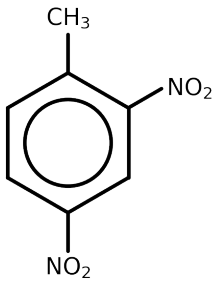
2,3-dinitromethylbenzene



2,6-dinitromethylbenzene



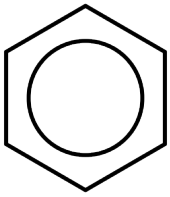
3,5-dinitromethylbenzene



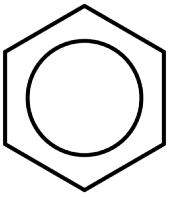
2,4-dinitromethylbenzene

(a) mechanism (use the whole width)

(b) isomer 5



(b) isomer 6



Self-check — I can…

- ☐ do a 6-mark mechanism question in exam conditions
- ☐ use a directing table I have never seen before
- ☐ explain phenol's reactivity in three technical sentences