

Aromatic Chemistry

Support Guide

small steps · big print · pictures · recipes



Kekulé: alternating bonds



Delocalised: a circle

This guide is for you if...

- the slides go too fast
- you like to see one thing at a time
- you want a recipe to follow for mechanisms and explanations
- you revise best with pictures and short sentences

Name: _____

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

Support pages

How to use this guide

This guide goes with the Aromatic Chemistry lessons. It says the same things as the slides, but in smaller steps, with fewer words and more pictures.

The 5 things you must know

1	Read ONE box at a time. Cover it. Say it out loud. Check.
2	Every lesson has: 5 must-know facts → a step-by-step recipe → a worked example → your turn → check yourself.
3	Words in bold are key words. They are all in the word mat at the back.
4	The recipe cards (page 'Mechanism recipe') work for EVERY mechanism in this topic. Cut them out and keep them.
5	If you are stuck in an exam question, use the 'Which recipe do I need?' page.

Colour	What it means
Blue box	a question to answer
Green box	an answer to check against
Amber box	a key word or a memory hook
Pink box	a common mistake — watch out!
Grey box	steps to follow in order

Which recipe do I need?

If the question says...	Use...	Page
'Draw the mechanism'	the 4-move recipe card	Mechanism recipe
'Name this compound'	the 3-step naming recipe	Lesson 2

If the question says...	Use...	Page
'Explain why benzene does not react with bromine'	the writing frame: benzene vs alkene	Writing frames
'Explain why phenol reacts more readily'	the writing frame: phenol	Writing frames
'Explain the role of the catalyst'	the writing frame: catalyst	Writing frames
'Suggest a two-step synthesis'	the 3-step planning recipe	Lesson 7
'Give the reagents and conditions'	the knowledge organiser table	Knowledge organiser

Lesson 1

Meet benzene

Spec 6.1.1 (a) (b) (f): Kekulé model vs delocalised model: p-orbital overlap → delocalised π -system · evidence for delocalisation: bond lengths, enthalpy change of hydrogenation, resistance to reaction · why benzene resists bromination compared with alkenes: delocalised vs localised π electron density

The 5 things you must know

1

Benzene is C_6H_6 : six carbon atoms in a flat, six-sided ring.



Kekulé: alternating bonds Delocalised: a circle

2

Kekulé drew alternating double bonds. The REAL ring has a circle: the electrons are delocalised (shared round the whole ring).

3

All six C–C bonds are the SAME length: 0.139 nm.



C=C 0.134 nm

C–C 0.153 nm



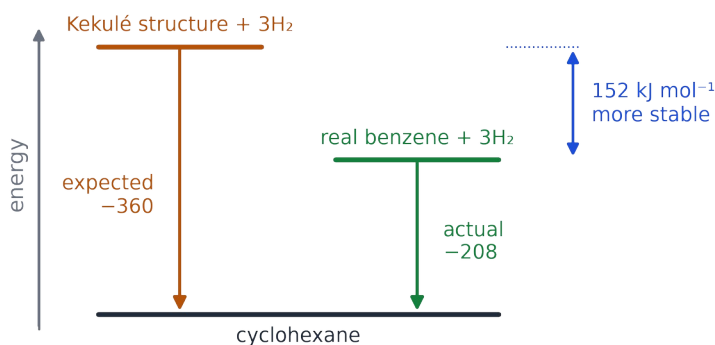
all 0.139 nm

Kekulé model predicts

X-ray diffraction shows

4

Benzene is MORE stable than Kekulé expected — by 152 kJ mol^{-1} .

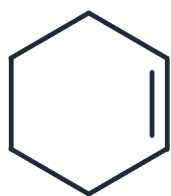


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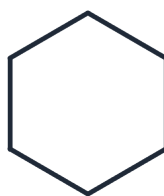
Benzene does NOT react with bromine water. Alkenes DO.



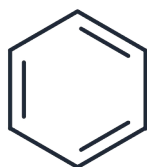
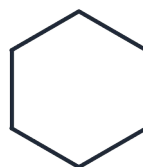
benzene

**How to explain the hydrogenation evidence (3 steps)****1**Step 1: Cyclohexene has ONE double bond. Adding H_2 gives -120 kJ mol^{-1} .

cyclohexene

 $+ \text{H}_2$ 

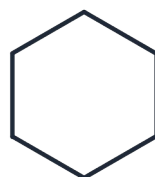
cyclohexane

 $\Delta H = -120 \text{ kJ mol}^{-1}$ **2**Step 2: Kekulé's benzene has THREE double bonds, so it SHOULD give $3 \times (-120) = -360 \text{ kJ mol}^{-1}$.cyclohexa-1,3,5-triene
(Kekulé) $+ 3\text{H}_2$ 

cyclohexane

expected $\Delta H = 3 \times (-120)$
 $= -360 \text{ kJ mol}^{-1}$ **3**Step 3: Real benzene gives only -208 kJ mol^{-1} . That is 152 kJ mol^{-1} LESS. So benzene is 152 kJ mol^{-1} MORE stable $\rightarrow$ the electrons are delocalised.

benzene

 $+ 3\text{H}_2$ 

cyclohexane

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

Why does benzene not decolourise bromine water?

I DO — read this worked example

In benzene the π electrons are delocalised over six carbons.

So the electron density between any two carbons is low.

Benzene cannot polarise the Br_2 molecule, so no electrophile forms and there is no reaction.

WE DO — fill in the gaps

In benzene the π electrons are _____ over six carbons.

So the electron density between any two carbons is _____.

Benzene cannot _____ the Br_2 molecule, so no _____ forms and there is no reaction.

YOU DO — your turn

Now YOU explain why cyclohexene DOES decolourise bromine water. Use: localised, high electron density, polarise, electrophile, addition.

Words to use: delocalised • low • polarise • electrophile

Watch out! Common mistakes

X People often write...	✓ What you should write
Benzene has three double bonds.	Benzene has NO separate double bonds — six delocalised electrons in a ring.
Benzene gives out more energy, so it is more stable.	Benzene gives out LESS energy. It is LOWER in energy, so MORE stable.
The circle is a bond.	The circle means six shared (delocalised) electrons.

Memory hook: Kekulé = alternate. Circle = share. • One-three-nine: every bond is 0.139!

Check yourself

1. What is the formula of benzene?	C₆H₆
2. How long is each C–C bond?	0.139 nm (all the same)
3. Does benzene decolourise bromine water?	No — it has no localised C=C bond to polarise Br₂

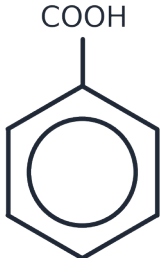
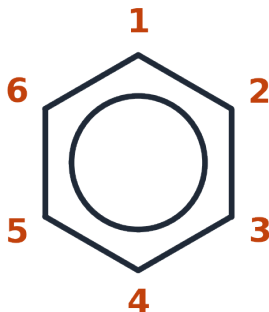
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Lesson 2

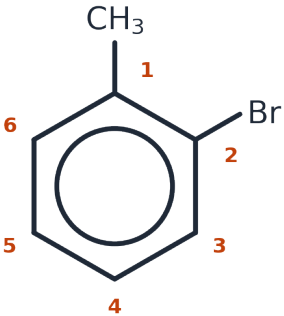
Naming aromatic compounds

Spec 6.1.1 (c): IUPAC rules for naming substituted aromatic compounds

The 5 things you must know

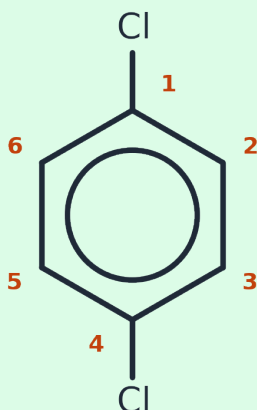
1	ONE group on the ring → group + benzene: chlorobenzene, nitrobenzene, methylbenzene.	
	 ethylbenzene  chlorobenzene  nitrobenzene	
2	FOUR special names to learn: phenol (OH), phenylamine (NH ₂), benzoic acid (COOH), benzaldehyde (CHO).	
	 benzoic acid  phenylamine  benzaldehyde  phenol	
3	TWO or more groups → number the ring, 1 to 6.	
4	Use the LOWEST numbers you can.	
5	Write the groups in ALPHABETICAL order: bromo, chloro, methyl, nitro.	

How to name a ring with two groups (3 steps)

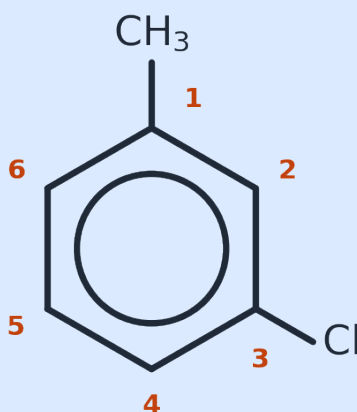
1	Step 1: Find the parent (methylbenzene, phenol, phenylamine, benzoic acid). Its group is on carbon 1.	
2	Step 2: Count round to the other group. Go the way that gives the SMALLEST number. Here bromine is on carbon 2 (not 6).	
3	Step 3: Write it: number – group – parent → 2-bromomethylbenzene.	

Naming: worked example

I DO — read this worked example



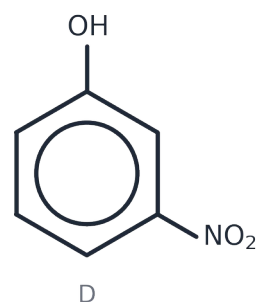
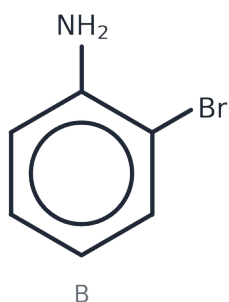
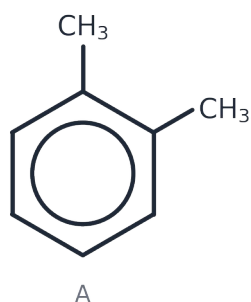
Two Cl groups, opposite each other. Same group twice → 'di'. Numbers 1 and 4.
Name: 1,4-dichlorobenzene.

WE DO — fill in the gaps

CH₃ on carbon ____ (methylbenzene is the parent). Cl on carbon _____. Name: _____-chloromethylbenzene.

YOU DO — your turn

Name compounds A, B, C and D in the picture below. (Answers in the check box.)

**Watch out! Common mistakes**

X People often write...	✓ What you should write
6-bromomethylbenzene	2-bromomethylbenzene — count the other way for the lowest number.
chloronitrobenzene	1-chloro-2-nitrobenzene — numbers AND alphabetical order.

✗ People often write...	✓ What you should write
benzylamine for $\text{C}_6\text{H}_5\text{NH}_2$	phenylamine.

Memory hook: Lowest numbers. Alphabetical letters. • PhenOL has the OH.

Check yourself

1. Name $\text{C}_6\text{H}_5\text{Cl}$.	chlorobenzene
2. Name $\text{C}_6\text{H}_5\text{OH}$.	phenol
3. Name the picture: A, B, C, D.	A 1,2-dimethylbenzene; B 2-bromophenylamine; C 4-chlorobenzoic acid; D 3-nitrophenol

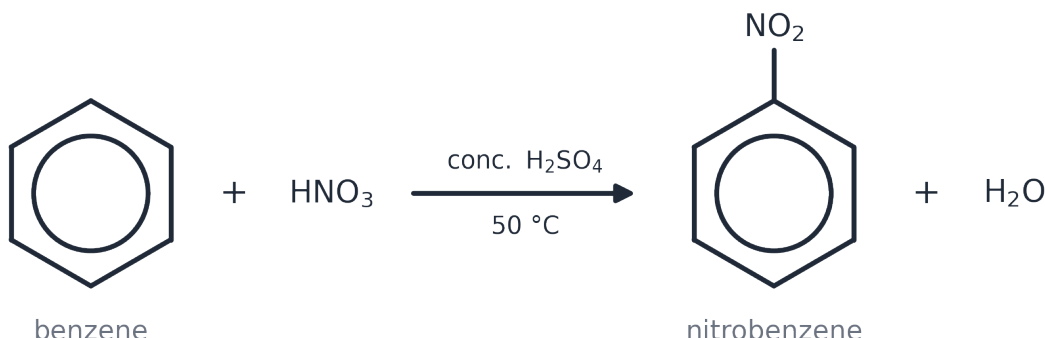
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Lesson 3

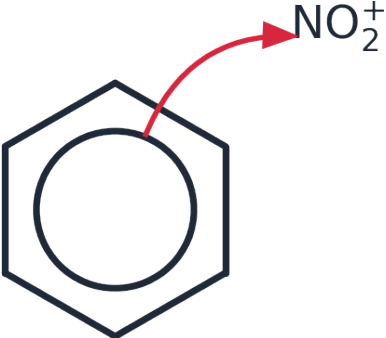
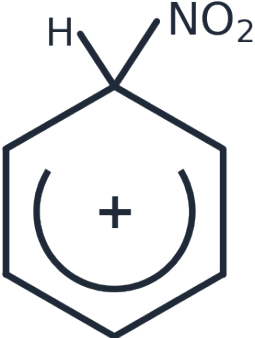
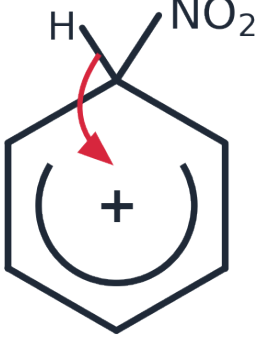
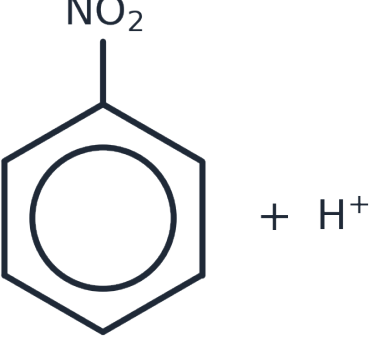
Nitration

Spec 6.1.1 (d)(i) (e): electrophilic substitution with conc. nitric acid + conc. sulfuric acid (nitration)
· the mechanism of electrophilic substitution for nitration and halogenation

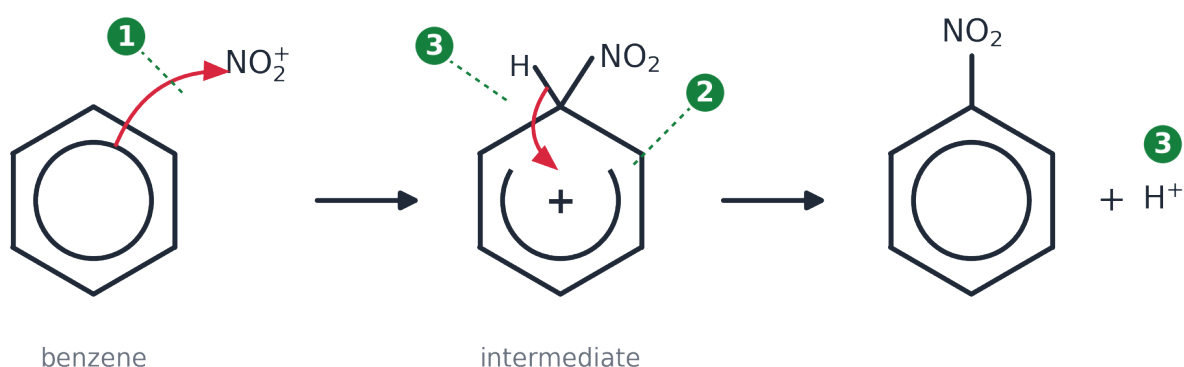
The 5 things you must know

1	Reagents: concentrated nitric acid + concentrated sulfuric acid (the catalyst).						
							
2	Temperature: 50 °C in a water bath. Hotter → a second NO ₂ goes on.						
3	The electrophile is NO ₂ ⁺ , the nitronium ion.						
	<table><tr><td>NO₂⁺</td><td>Br⁺</td><td>CH₃CO⁺</td></tr><tr><td>nitration</td><td>bromination</td><td>acylation</td></tr></table>	NO ₂ ⁺	Br ⁺	CH ₃ CO ⁺	nitration	bromination	acylation
NO ₂ ⁺	Br ⁺	CH ₃ CO ⁺					
nitration	bromination	acylation					
4	Make it: HNO ₃ + H ₂ SO ₄ → NO ₂ ⁺ + HSO ₄ ⁻ + H ₂ O						
5	Product: nitrobenzene + water. Catalyst back: H ⁺ + HSO ₄ ⁻ → H ₂ SO ₄						

The mechanism in 4 moves

 MOVE 1: Curly arrow. Tail ON the circle. Head TOUCHING the N of NO_2^+ (not an O).	 MOVE 2: The intermediate. Open the circle into a horseshoe that stops at the two carbons next to the top carbon. Write + INSIDE it. H and NO_2 on the SAME carbon.
 MOVE 3: Curly arrow. Tail on the MIDDLE of the C-H bond (not on the H). Head INTO the ring, towards the +.	 MOVE 4: Draw the product (nitrobenzene) + H^+.

Then write the catalyst step: $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$

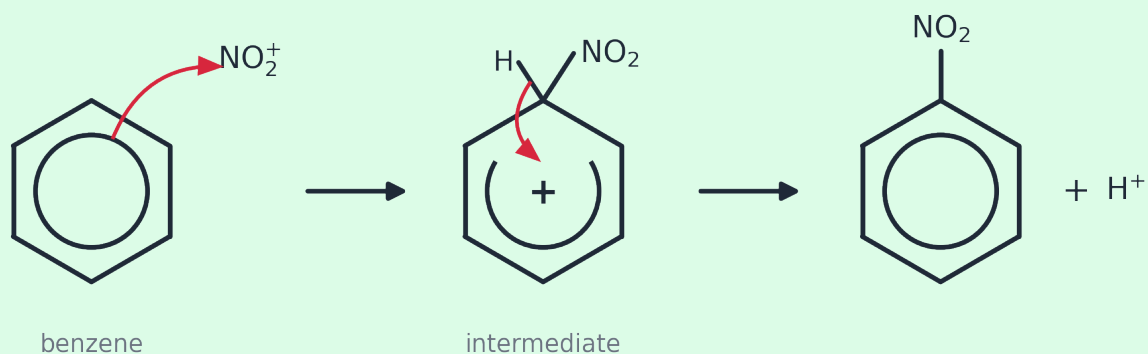


Where the 3 marks are: ① arrow tail on the circle, head on the N · ② horseshoe + plus + H and NO_2 on the same carbon · ③ arrow from the C-H bond into the ring, and H^+ .

Mark	What the examiner must SEE	Loses the mark if...
1	Arrow tail ON the circle; head TOUCHING the N of NO_2^+	the head is on an O; the arrow points the other way; the tail is on the hexagon edge
2	Horseshoe stops at the carbons next to the top carbon; + INSIDE it; H and NO_2 on the SAME carbon	the circle is still complete; the + is missing or on the wrong atom; no H drawn
3	Arrow tail on the MIDDLE of the C–H bond; head INTO the ring; nitrobenzene + H^+ written	the arrow starts at the H; no H^+ in the products

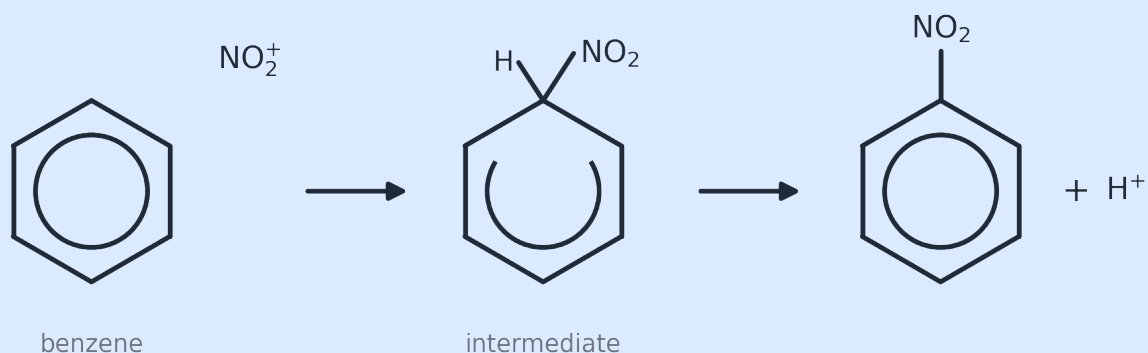
The mechanism: I do → we do → you do

I DO — read this worked example



Here is the full mechanism. Look at where each arrow STARTS and ENDS.

WE DO — fill in the gaps

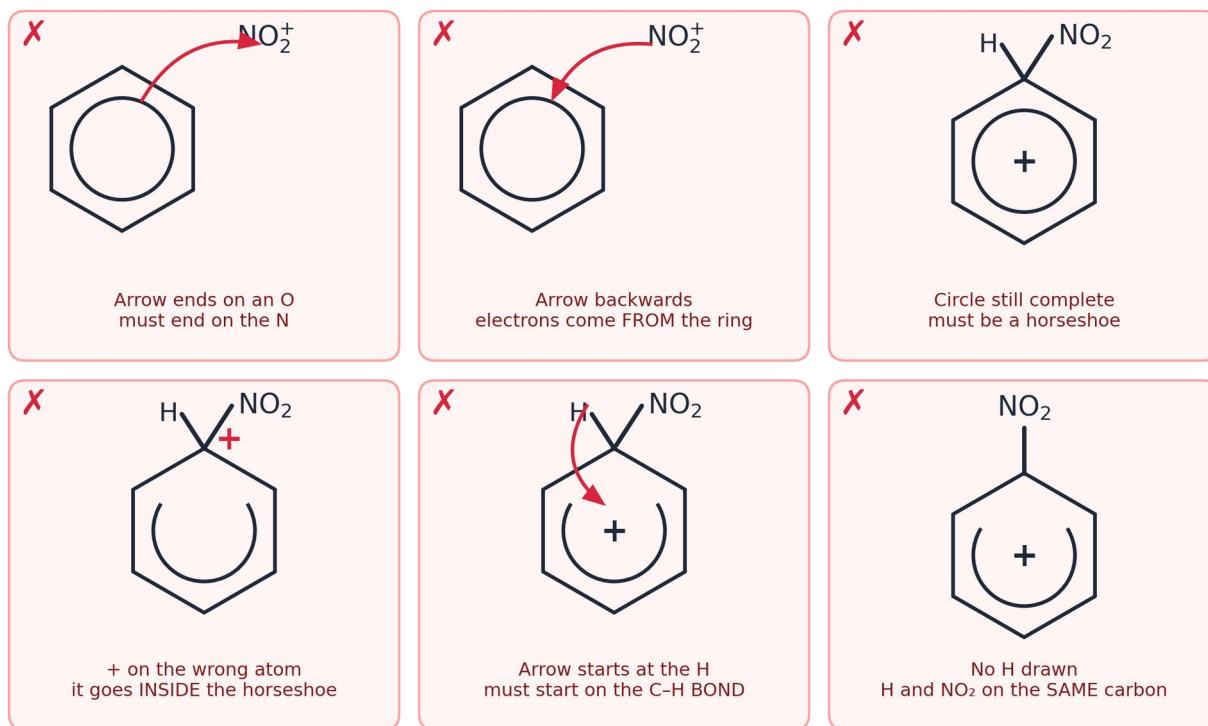


Add the two curly arrows and the + charge to this skeleton.

YOU DO — your turn

Draw the whole mechanism from memory on paper. Use the 4-move recipe card. Then check it with the checklist below.

Checklist — tick each one on YOUR mechanism	✓
Equation for making the electrophile (e.g. $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$)	
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 ($\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$ or $\text{H}^+ + \text{FeBr}_4^- \rightarrow \text{FeBr}_3 + \text{HBr}$)	



Six ways to lose a mark. Cover the captions and say what is wrong with each one.

Role of the catalyst (2 marks)

H₂SO₄ is a catalyst because it is _____ in step 1, where it makes _____.
It is _____ at the end: H⁺ + HSO₄⁻ → H₂SO₄.

Word bank: used up • NO₂⁺ • regenerated

Watch out! Common mistakes

X People often write...	✓ What you should write
Arrow from NO ₂ ⁺ to the ring.	Arrow from the RING to the N.
Intermediate with no + charge.	Horseshoe AND a + charge.
Arrow starting on the H atom.	Arrow starting on the C-H BOND.

Memory hook: Ring gives, ring gets back. • Fifty for one NO₂, seventy for two.

Check yourself

1. What is the electrophile in nitration?

NO₂⁺ (nitronium ion)

2. What are the conditions?	conc. HNO_3 + conc. H_2SO_4, 50 °C
3. Which acid is the catalyst?	sulfuric acid, H_2SO_4

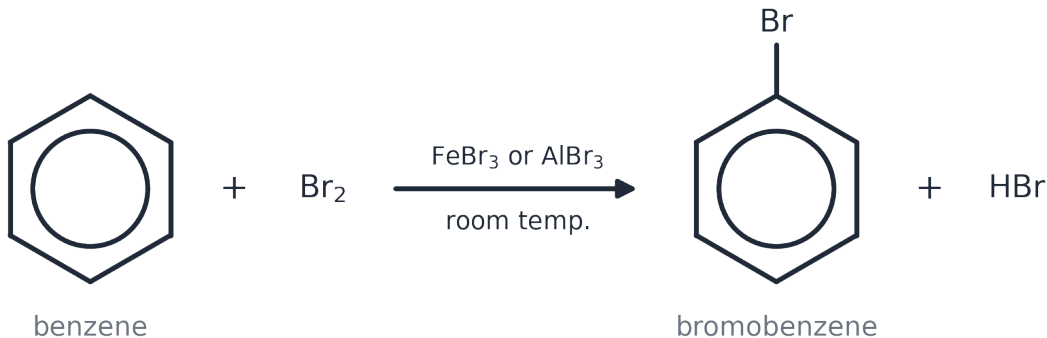
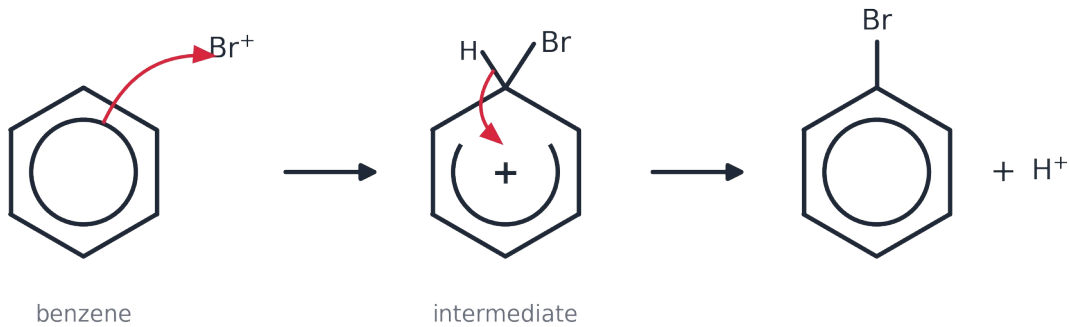
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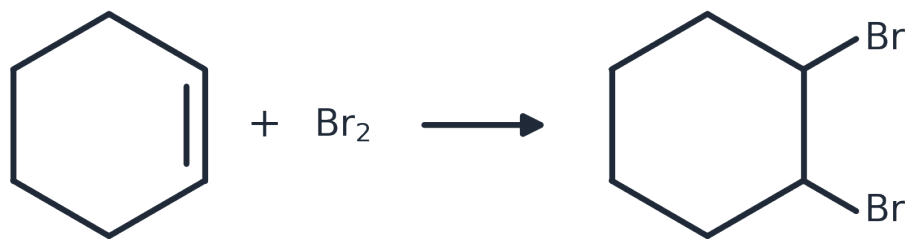
Lesson 4

Halogenation

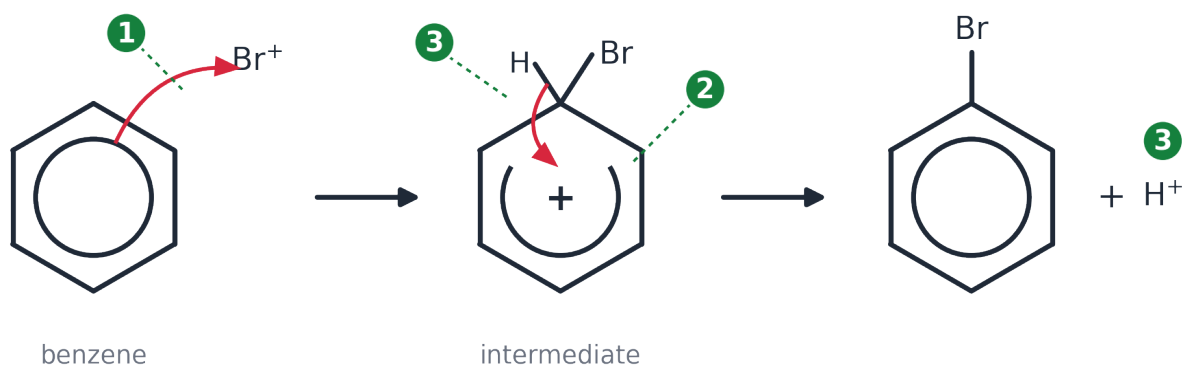
Spec 6.1.1 (d)(ii) (e) (f): electrophilic substitution with a halogen + a halogen carrier · the mechanism of electrophilic substitution for nitration and halogenation · why benzene resists bromination compared with alkenes: delocalised vs localised π electron density

The 5 things you must know

1	Benzene + Br ₂ needs a halogen carrier: FeBr ₃ , AlCl ₃ or iron filings.
	
2	The carrier makes the electrophile Br ⁺ : Br ₂ + FeBr ₃ → Br ⁺ + FeBr ₄ ⁻
3	Then the SAME 4-move mechanism — just swap NO ₂ ⁺ for Br ⁺ .
	
4	Catalyst back: H ⁺ + FeBr ₄ ⁻ → FeBr ₃ + HBr
5	Alkenes react with Br ₂ with NO catalyst (addition). Benzene does not (needs a carrier; substitution).



electrophilic ADDITION — no catalyst — bromine decolourised



Same 3 marks: ① tail on the circle, head touching Br^+ · ② horseshoe, + inside, H and Br on the same carbon · ③ arrow from the C–H bond into the ring, + H^+ .

The three steps EVERY halogenation needs

1	Step 1: Make the electrophile: $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$
2	Step 2: Substitution: the 4-move recipe (arrow in, horseshoe +, arrow back, product + H^+).
3	Step 3: Catalyst back: $\text{H}^+ + \text{FeBr}_4^- \rightarrow \text{FeBr}_3 + \text{HBr}$

Chlorination with AlCl_3

I DO — read this worked example

Step 1: $\text{Cl}_2 + \text{AlCl}_3 \rightarrow \text{Cl}^+ + \text{AlCl}_4^-$. Step 2: 4-move recipe with $\text{Cl}^+ \rightarrow$ chlorobenzene + H^+ . Step 3: $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl}$.

WE DO — fill in the gaps

Step 1: $\text{Cl}_2 + \text{AlCl}_3 \rightarrow \underline{\hspace{2cm}} + \underline{\hspace{2cm}}$. Step 2: recipe $\rightarrow \underline{\hspace{2cm}} + \text{H}^+$.
 Step 3: $\text{H}^+ + \underline{\hspace{2cm}} \rightarrow \text{AlCl}_3 + \underline{\hspace{2cm}}$.

YOU DO — your turn

Write all three steps for chlorination using FeCl_3 instead of AlCl_3 .

Alkene vs benzene with bromine (4 marks)

1. In an alkene the π electrons are _____ between two carbons, so the electron density is _____.
2. This _____ the Br_2 molecule: $\text{Br } \delta^+$ is the _____.
3. In benzene the π electrons are _____ over six carbons, so the electron density is _____.
4. Benzene cannot _____ Br_2 , so a _____ is needed to make Br^+ .

Word bank: localised • high • polarises • electrophile • delocalised • lower • polarise • halogen carrier

Watch out! Common mistakes

X People often write...	✓ What you should write
Benzene decolourises bromine water.	It does NOT — unless a halogen carrier is used.
FeBr_3 is the electrophile.	Br^+ is the electrophile. FeBr_3 is the catalyst that MAKES it.
Bromine ADDS to benzene.	Bromine SUBSTITUTES for an H (the ring stays).

Memory hook: The CARRIER makes the PLUS. • Alkene: adds. Arene: swaps.

Check yourself

1. Name three halogen carriers.	FeBr₃, AlCl₃, iron (also AlBr₃, FeCl₃)
2. Write the equation that makes Br ⁺ .	Br₂ + FeBr₃ → Br⁺ + FeBr₄⁻
3. What do you SEE when bromine water is added to benzene?	No change — stays orange

Cover the green column with your hand. Say the answer. Then check.

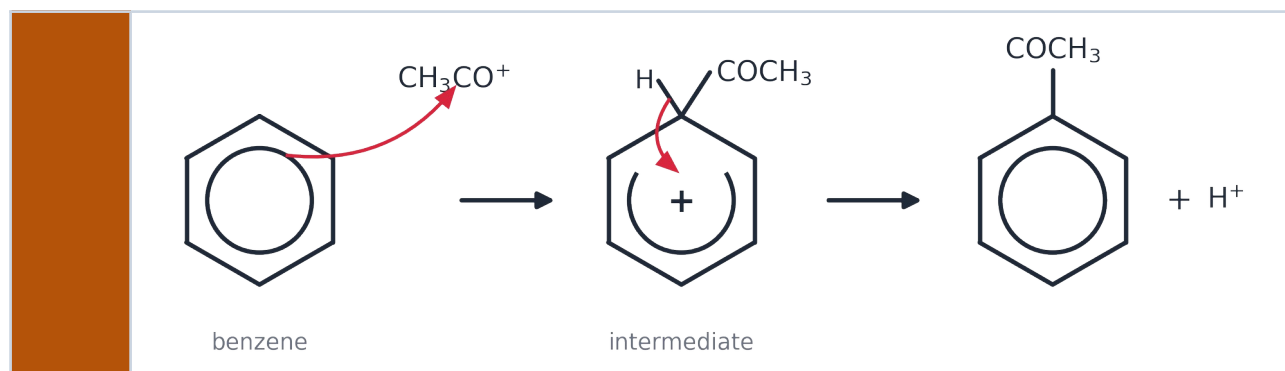
Lesson 5

Friedel–Crafts

Spec 6.1.1 (d)(iii) (g): Friedel–Crafts: haloalkane or acyl chloride + halogen carrier; C–C bond formation for synthesis · interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms

The 5 things you must know

1	Friedel–Crafts reactions ADD CARBON to the ring: a new C–C bond.
2	Alkylation: haloalkane + $\text{AlCl}_3 \rightarrow$ alkylbenzene. Example: benzene + $\text{C}_2\text{H}_5\text{Cl} \rightarrow$ ethylbenzene + HCl .
3	Acylation: acyl chloride + $\text{AlCl}_3 \rightarrow$ a ketone. Example: benzene + $\text{CH}_3\text{COCl} \rightarrow$ phenylethanone + HCl .
4	Electrophiles: C_2H_5^+ (alkylation) and CH_3CO^+ (acylation). AlCl_3 makes them: $\text{C}_2\text{H}_5\text{Cl} + \text{AlCl}_3 \rightarrow \text{C}_2\text{H}_5^+ + \text{AlCl}_4^-$
5	Same 4-move mechanism. Catalyst back: $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl}$



How to predict the product (3 steps)

- 1 Step 1: Cross out the Cl on the reagent ($\text{CH}_3\text{CO}-\text{Cl} \rightarrow \text{CH}_3\text{CO}$).
- 2 Step 2: Join what is left onto the ring where an H was.
- 3 Step 3: Write HCl as the other product.

Predict the product

I DO — read this worked example

benzene + CH_3Cl (AlCl_3) $\rightarrow$ methylbenzene + HCl

WE DO — fill in the gaps

benzene + CH_3COCl (AlCl_3) $\rightarrow$ _____ + HCl

YOU DO — your turn

benzene + $\text{C}_2\text{H}_5\text{Cl}$ (AlCl_3) $\rightarrow$? and benzene + $\text{C}_6\text{H}_5\text{COCl}$ (AlCl_3) $\rightarrow$?

Watch out! Common mistakes

✗ People often write...	✓ What you should write
The product of acylation is an alcohol.	It is a KETONE ($\text{C}=\text{O}$ next to the ring).
AlCl_3 ends up in the product.	AlCl_3 is regenerated — it is a catalyst.

X People often write...	✓ What you should write
Friedel–Crafts uses a halogen (Br_2).	It uses a HALOALKANE or an ACYL CHLORIDE (+ AlCl_3).

Memory hook: Alkyl = a chain. Acyl = $\text{C}=\text{O}$. • Cross out the Cl, join the rest.

Check yourself

1. What type of bond does Friedel–Crafts make?	a C–C bond to the ring
2. Name the product of benzene + CH_3COCl .	phenylethanone
3. What is the electrophile in acylation with CH_3COCl ?	CH_3CO^+

Cover the green column with your hand. Say the answer. Then check.

Lesson 6

Phenol

Spec 6.1.1 (h) (i) (j): weak acidity of phenols: reacts with NaOH, no reaction with carbonates · phenol + bromine → 2,4,6-tribromophenol; phenol + dilute nitric acid → 2-nitrophenol and 4-nitrophenol · phenol is more easily substituted than benzene: electron pair donated from an oxygen p-orbital into the π -system

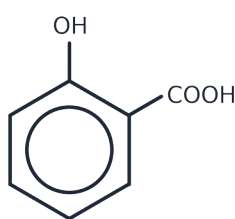
The 5 things you must know

1

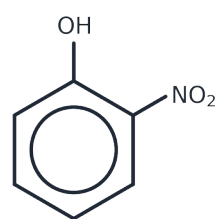
Phenol = an OH group DIRECTLY on the ring. (OH on a side chain = an alcohol.)



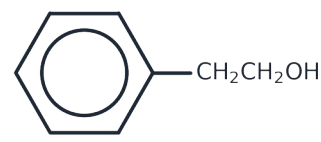
phenol



2-hydroxybenzoic acid



2-nitrophenol



2-phenylethanol

2

Phenol is a WEAK acid: it reacts with NaOH (yes) but NOT with Na_2CO_3 (no fizz).



phenol

+

NaOH



sodium phenoxide

+

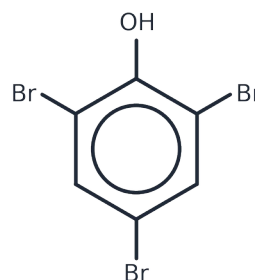
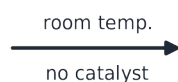
 H_2O **3**

Phenol + bromine water → white precipitate of 2,4,6-tribromophenol. NO catalyst needed.



phenol

+

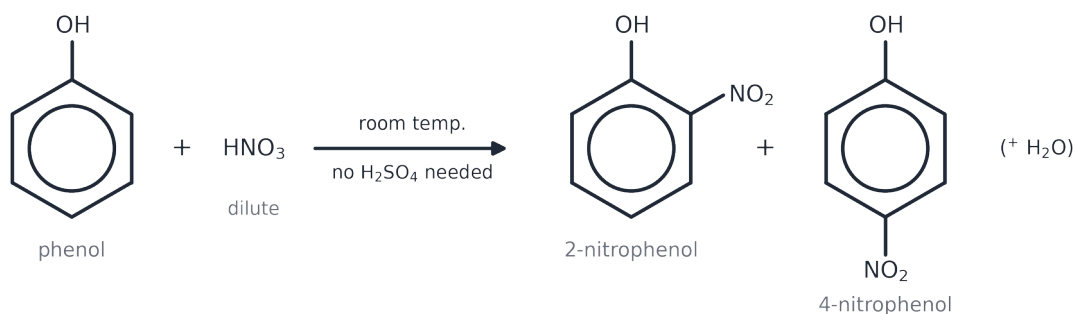
 3Br_2 2,4,6-tribromophenol
(white precipitate)

+

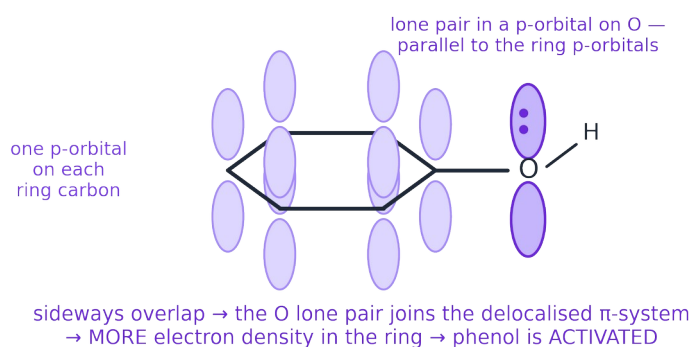
 3HBr

4

Phenol + DILUTE nitric acid → 2-nitrophenol and 4-nitrophenol.

**5**

Why more reactive than benzene? A lone pair on the O goes into the ring → more electron density.



How to explain why phenol is MORE reactive (3 steps)

1

Step 1: A lone pair on the oxygen is in a p-orbital.

2

Step 2: It is delocalised into the ring, so the ring's electron density goes UP.

3Step 3: The ring can now polarise Br_2 , so it reacts with NO catalyst.

Phenol vs benzene

I DO — read this worked example

Phenol reacts with bromine water without a catalyst because an oxygen lone pair is delocalised into the ring. This increases the electron density, so the ring polarises Br_2 .

WE DO — fill in the gaps

Phenol reacts with bromine water without a catalyst because an oxygen _____ is _____ into the ring. This _____ the electron density, so the ring _____ Br_2 .

YOU DO — your turn

Now explain why phenol reacts with DILUTE nitric acid but benzene needs CONCENTRATED nitric AND sulfuric acid.

Words to use: lone pair • delocalised • increases • polarises

	Benzene + Br_2	Phenol + Br_2
Catalyst?	YES — halogen carrier	NO
What you see	nothing	orange → colourless + white solid
How many Br?	one	three (2, 4, 6)
Product	bromobenzene	2,4,6-tribromophenol

Watch out! Common mistakes

✗ People often write...	✓ What you should write
Phenol fizzes with sodium carbonate.	NO reaction — phenol is too weak an acid.
One Br goes on phenol.	THREE Br go on: positions 2, 4 and 6.
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ is a phenol.	The OH is on a side chain → it is an ALCOHOL.

Memory hook: Phenol: NaOH yes, carbonate no. • Phenol + Br_2 : no catalyst, three Br, white solid.

Check yourself

1. Does phenol react with Na_2CO_3 ?	No
2. Name the product of phenol + excess bromine water.	2,4,6-tribromophenol (white precipitate)
3. Which acid nitrates phenol?	DILUTE nitric acid (no H_2SO_4 needed)

Cover the green column with your hand. Say the answer. Then check.

Lesson 7

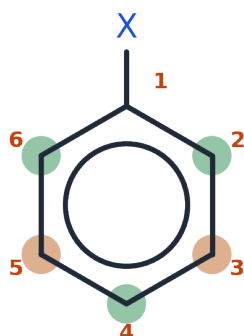
Directing groups

Spec 6.1.1 (k) (l): OH and NH₂ (electron-donating) direct to 2- and 4-; NO₂ (electron-withdrawing) directs to 3- · predicting substitution products from directing effects; importance to organic synthesis

The 5 things you must know

1

A group already on the ring decides WHERE the next group goes.



2, 4 (and 6): 'ortho / para'
— electron-DONATING groups
(OH, NH₂) send new groups here

3 (and 5): 'meta'
— electron-WITHDRAWING groups
(NO₂) send new groups here

2

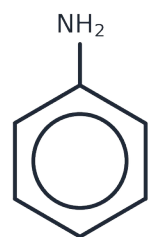
OH and NH₂ GIVE electrons → the new group goes to position 2 or 4.

3

NO₂ TAKES electrons → the new group goes to position 3.

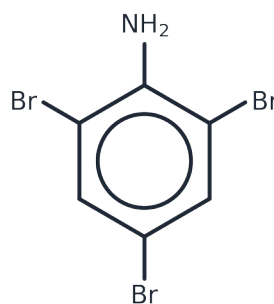
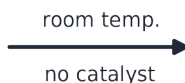
4

OH and NH₂ make the ring MORE reactive. NO₂ makes it LESS reactive.



phenylamine

+

3Br₂

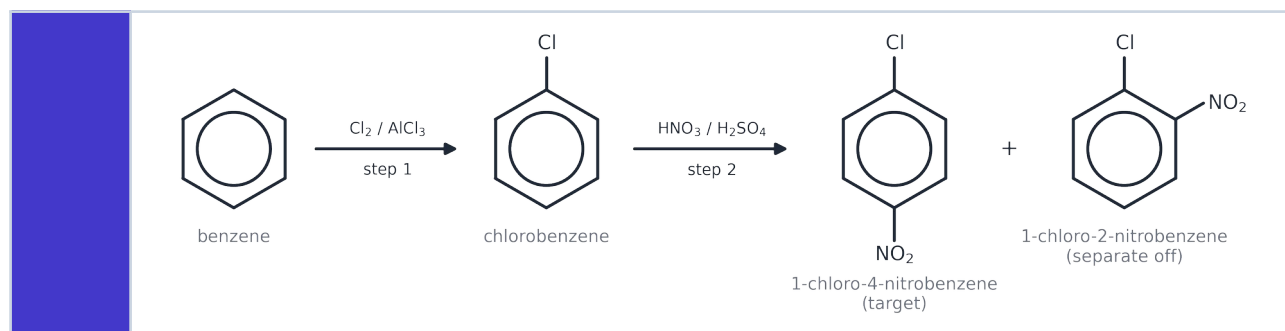
2,4,6-tribromophenylamine

+

3HBr

5

In a two-step synthesis, put on FIRST the group that sends the second one to the right place.



How to plan a two-step synthesis (3 steps)

1	Step 1: Look at the target. Are the two groups 1,2 or 1,4 apart? → you need a 2,4-director on first. Are they 1,3 apart? → you need a 3-director on first.
2	Step 2: Put that group on first (write the reagents and conditions).
3	Step 3: Add the second group (reagents and conditions). Say if you get a mixture to separate.

Plan it

I DO — read this worked example

Target: 1-chloro-4-nitrobenzene (groups 1,4 apart). Cl is a 2,4-director → Cl FIRST ($\text{Cl}_2/\text{AlCl}_3$), THEN nitrate (conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$, 50 °C).

WE DO — fill in the gaps

Target: 3-bromonitrobenzene (groups 1,3 apart). NO_2 is a 3-director → _____ FIRST (_____), THEN _____ ($\text{Br}_2/\text{FeBr}_3$).

YOU DO — your turn

Target: 4-bromonitrobenzene. Which group first? Give the reagents for both steps.

Group on the ring	Gives or takes electrons?	Sends the new group to...
-OH	gives	2 and 4
-NH ₂	gives	2 and 4
-NO ₂	takes	3

Watch out! Common mistakes

X People often write...	✓ What you should write
OH sends the next group to 3.	OH → 2 and 4. NO ₂ → 3.
The order of the steps does not matter.	Wrong order = wrong isomer!
Position 6 is different from position 2.	2 and 6 are the SAME (mirror images) — always say 2.

Memory hook: Givers go 2,4. Takers go 3.

Check yourself

1. Where does OH send the next group?	2 and 4
2. Where does NO ₂ send the next group?	3
3. To make 1-chloro-4-nitrobenzene, which group goes on first?	Cl (it is 2,4-directing)

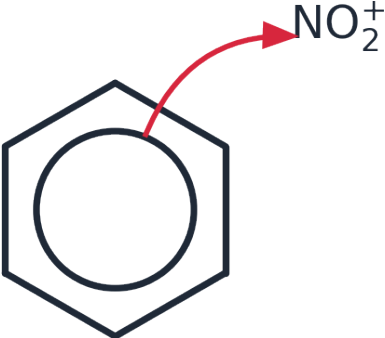
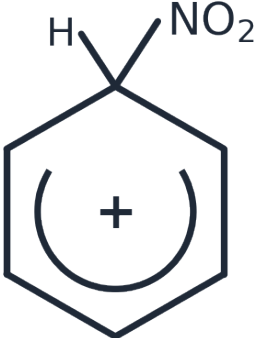
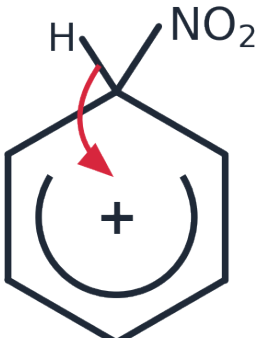
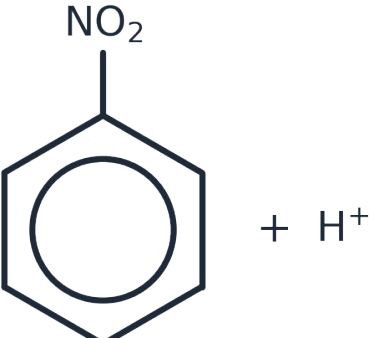
Cover the green column with your hand. Say the answer. Then check.

Support pages

Mechanism recipe cards

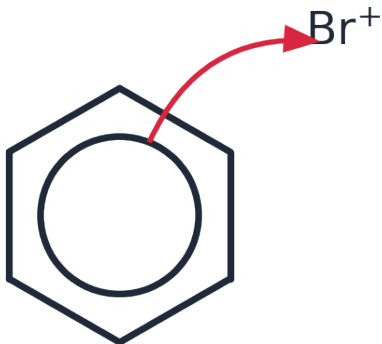
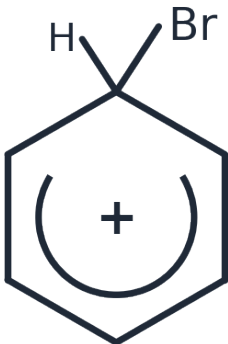
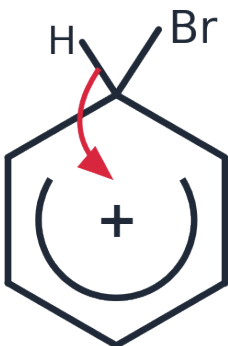
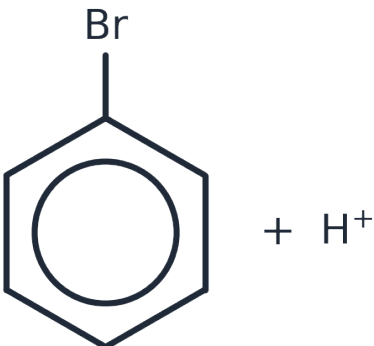
Cut these out. They work for EVERY electrophilic substitution in this topic: just swap the electrophile.

Nitration (electrophile NO_2^+)

 MOVE 1: arrow — tail ON the circle, head TOUCHING the N of NO_2^+	 MOVE 2: horseshoe (stops either side of the carbon with H and NO_2) + plus INSIDE; H and NO_2 on the SAME carbon
 MOVE 3: arrow — tail on the MIDDLE of the C-H bond, head INTO the ring	 MOVE 4: product + H^+

Before: $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$. **After:** $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$

Bromination (electrophile Br⁺)

 MOVE 1: arrow — tail ON the circle, head TOUCHING Br⁺	 MOVE 2: horseshoe (stops either side of the carbon with H and Br) + plus INSIDE; H and Br on the SAME carbon
 MOVE 3: arrow — tail on the MIDDLE of the C–H bond, head INTO the ring	 MOVE 4: bromobenzene + H⁺

Before: $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$. **After:** $\text{H}^+ + \text{FeBr}_4^- \rightarrow \text{FeBr}_3 + \text{HBr}$

The three marks, in the examiner's words. Say them until you can say them in your sleep.

Mark	The examiner must see
1 · Curly arrow from the delocalised ring to N of NO₂⁺	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.

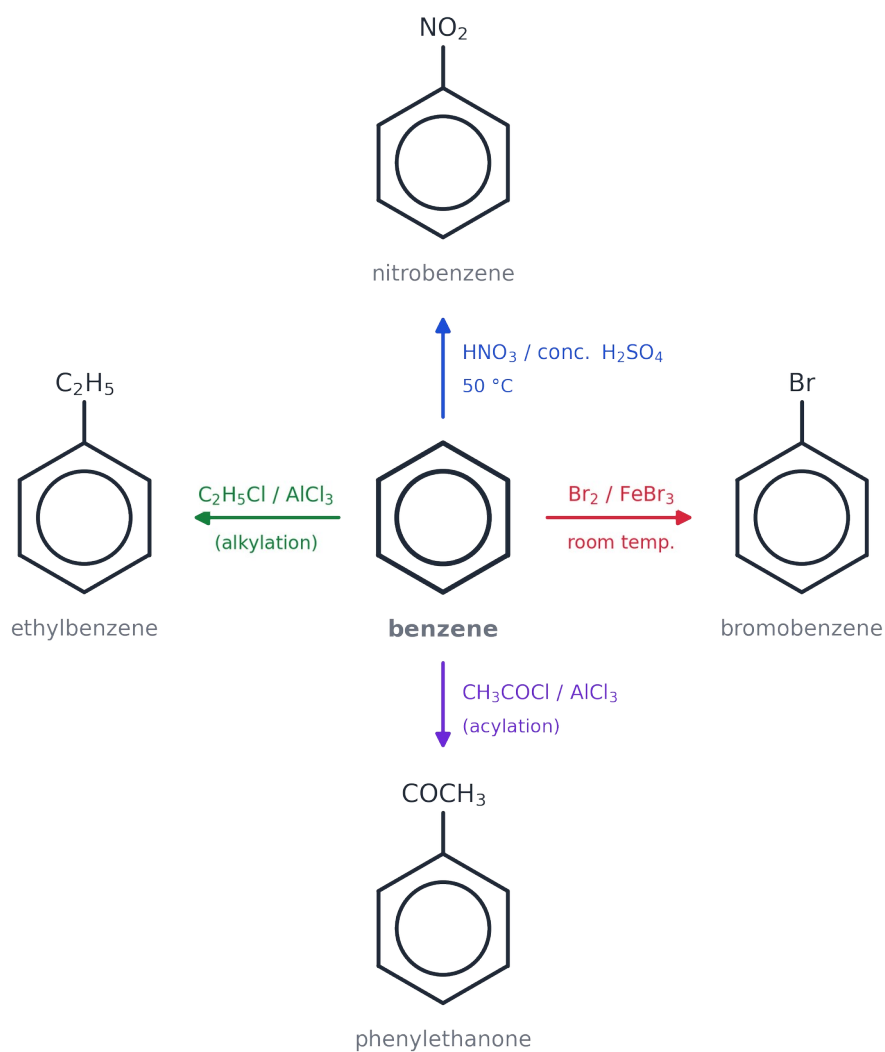
Mark	The examiner must see
3 · Curly arrow from the C–H bond into the ring, and H⁺ leaves	Tail on the MIDDLE of the C–H bond (a bond is breaking — never on the H atom). Head pointing into the ring, towards the +, to re-form the circle. Products: nitrobenzene + H ⁺ .

Where does arrow 1 go for the other electrophiles? Br⁺: the Br. Cl⁺: the Cl. CH₃CO⁺: the C of the C=O (it carries the +). SO₃: the S (δ+). Always the atom with the positive charge.

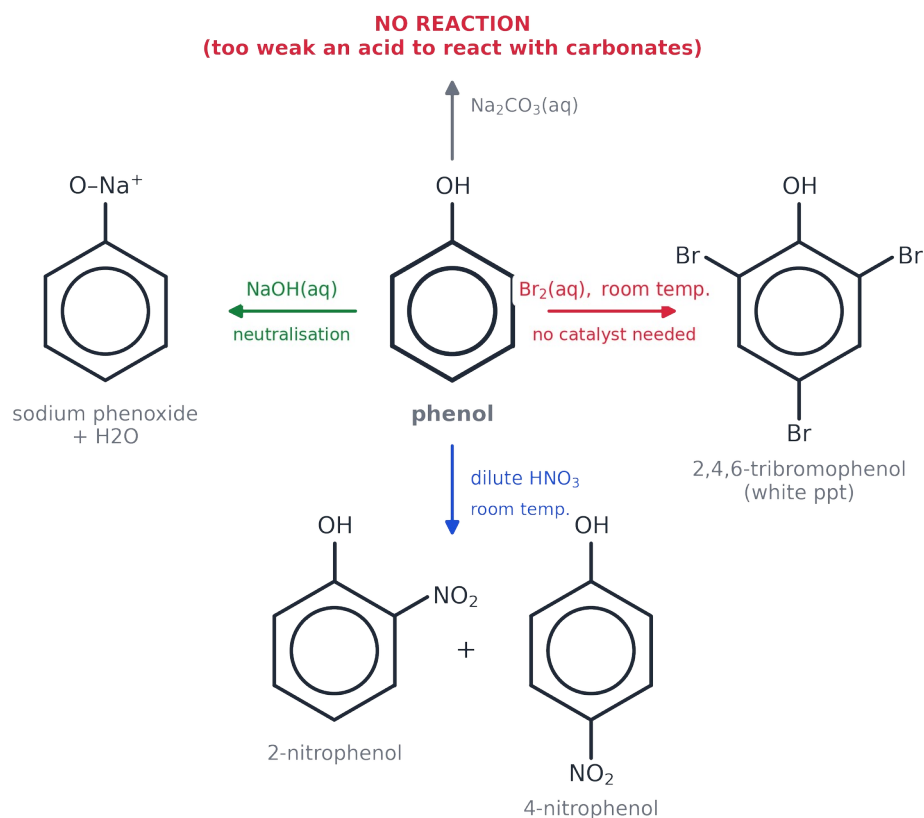
Reaction	Electrophil e	How it is made	Catalyst back
nitration	NO ₂ ⁺	HNO ₃ + H ₂ SO ₄ → NO ₂ ⁺ + HSO ₄ [−] + H ₂ O	H ⁺ + HSO ₄ [−] → H ₂ SO ₄
bromination	Br ⁺	Br ₂ + FeBr ₃ → Br ⁺ + FeBr ₄ [−]	H ⁺ + FeBr ₄ [−] → FeBr ₃ + HBr
chlorination	Cl ⁺	Cl ₂ + AlCl ₃ → Cl ⁺ + AlCl ₄ [−]	H ⁺ + AlCl ₄ [−] → AlCl ₃ + HCl
alkylation	C ₂ H ₅ ⁺	C ₂ H ₅ Cl + AlCl ₃ → C ₂ H ₅ ⁺ + AlCl ₄ [−]	H ⁺ + AlCl ₄ [−] → AlCl ₃ + HCl
acylation	CH ₃ CO ⁺	CH ₃ COCl + AlCl ₃ → CH ₃ CO ⁺ + AlCl ₄ [−]	H ⁺ + AlCl ₄ [−] → AlCl ₃ + HCl

Support pages

Knowledge organiser



Benzene: four reactions, one mechanism.



Phenol: weak acid, activated ring.

Reaction	Reagents	Conditions	Product
nitration	conc. HNO_3 + conc. H_2SO_4	50 °C, water bath	nitrobenzene + H_2O
bromination	Br_2 + FeBr_3 (halogen carrier)	room temperature	bromobenzene + HBr
chlorination	Cl_2 + AlCl_3	room temperature	chlorobenzene + HCl
alkylation	$\text{C}_2\text{H}_5\text{Cl}$ + AlCl_3	warm	ethylbenzene + HCl
acylation	CH_3COCl + AlCl_3	warm	phenylethanone + HCl
phenol + NaOH	NaOH(aq)	room temperature	sodium phenoxide + H_2O
phenol + Na_2CO_3	—	—	NO REACTION
phenol + Br_2	bromine water	room temp., no catalyst	2,4,6-tribromophenol (white ppt) + 3HBr

Reaction	Reagents	Conditions	Product
phenol + HNO₃	DILUTE nitric acid	room temperature	2-nitrophenol + 4-nitrophenol

Number to remember	What it is
0.139 nm	every C–C bond in benzene (C–C 0.153, C=C 0.134)
152 kJ mol⁻¹	how much more stable benzene is than Kekulé's structure
–208 kJ mol⁻¹	enthalpy change of hydrogenation of benzene (expected –360)
50 °C	nitration temperature
2, 4 / 3	where OH & NH ₂ / NO ₂ send the next group
120°	bond angle in benzene

Support pages

Writing frames for the 'explain' questions

Frame 1 — Why is benzene more stable than the Kekulé structure? (3 marks)

The Kekulé structure has three C=C bonds, so its enthalpy of hydrogenation should be $3 \times (-120) = \underline{\hspace{2cm}}$ kJ mol⁻¹.

The actual value for benzene is $\underline{\hspace{2cm}}$ kJ mol⁻¹.

Benzene releases $\underline{\hspace{2cm}}$ kJ mol⁻¹ LESS energy, so it is MORE $\underline{\hspace{2cm}}$, because the electrons are $\underline{\hspace{2cm}}$.

Word bank: -360 • -208 • 152 • stable • delocalised

Frame 2 — Why does benzene not react with bromine, when an alkene does? (4 marks)

In an alkene the π electrons are $\underline{\hspace{2cm}}$, so the electron density is $\underline{\hspace{2cm}}$.

The alkene $\underline{\hspace{2cm}}$ Br₂, making Br δ^+ the $\underline{\hspace{2cm}}$.

In benzene the π electrons are $\underline{\hspace{2cm}}$ over six carbons, so the electron density is $\underline{\hspace{2cm}}$.

Benzene cannot $\underline{\hspace{2cm}}$ Br₂, so no electrophile forms without a $\underline{\hspace{2cm}}$.

Word bank: localised • high • polarises • electrophile • delocalised • lower • polarise • halogen carrier

Frame 3 — Why does phenol react more readily than benzene? (3 marks)

A $\underline{\hspace{2cm}}$ on the oxygen is in a $\underline{\hspace{2cm}}$.

It is $\underline{\hspace{2cm}}$ into the ring's π -system, so the electron density of the ring $\underline{\hspace{2cm}}$.

The ring is more susceptible to attack: it can $\underline{\hspace{2cm}}$ Br₂ without a catalyst.

Word bank: lone pair • p-orbital • delocalised • increases • polarise

Frame 4 — Explain the role of the catalyst (2 marks)

_____ is used up in step 1 to make the electrophile _____.

It is _____ in the last step: _____.

Word bank: H_2SO_4 (or AlCl_3 / FeBr_3) • NO_2^+ (or Br^+ ...) • regenerated • $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$

Frame 5 — Why must the steps be done in this order? (2 marks)

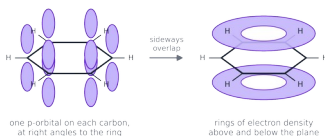
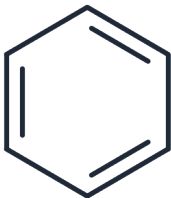
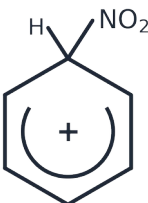
_____ must go on first because it directs the second group to position _____.

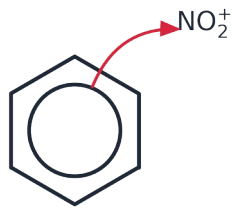
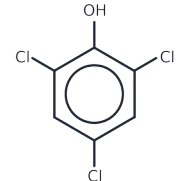
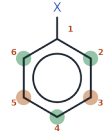
If _____ went on first it would direct to position _____, giving the _____ isomer.

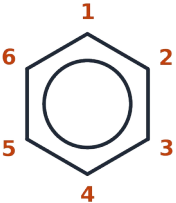
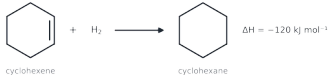
Word bank: Cl / the 2,4-director • 4 (and 2) • NO_2 • 3 • wrong

Support pages

Word mat

Word	What it means	Picture
benzene	C_6H_6 — a flat ring of six carbons with six delocalised electrons	
arene / aromatic	a compound that contains a benzene ring	
delocalised	electrons shared over several atoms, not stuck in one bond	
π-system	the ring of electron density above and below the benzene ring	
p-orbital	the orbital each carbon uses to make the π -system	
Kekulé structure	benzene drawn with alternating double bonds	
electrophile	a species that accepts a pair of electrons (E^+)	NO_2^+ nitration Br^+ bromination CH_3CO^+ acylation
electrophilic substitution	an electrophile swaps places with an H on the ring	
intermediate	the ring with a horseshoe and a + charge, halfway through the mechanism	

Word	What it means	Picture
curly arrow	shows a PAIR of electrons moving	
catalyst	speeds up the reaction and is regenerated at the end	
halogen carrier	the catalyst (FeBr_3 , AlCl_3 , Fe) that makes Br^+ or Cl^+	
nitronium ion	NO_2^+ , the electrophile in nitration	
Friedel–Crafts	alkylation or acylation: adds carbon to the ring using AlCl_3	
acyl chloride	RCOCl — used in acylation to make a ketone	
phenol	OH directly on the ring; a weak acid	 TCP (2,4,6-trichlorophenol)
phenoxide ion	$\text{C}_6\text{H}_5\text{O}^-$ — phenol after it loses H^+	
weak acid	only partly dissociates in water	
precipitate	a solid that forms in a solution (phenol + $\text{Br}_2 \rightarrow$ white ppt)	
directing group	a group on the ring that decides where the next group goes	 2, 4 (and 6): 'ortho / para' — electron-DONATING groups (OH, NH_2) send new groups here 3 (and 5): 'meta' — electron-WITHDRAWING groups (NO_2) send new groups here
activating	makes the ring MORE reactive (OH, NH_2)	
deactivating	makes the ring LESS reactive (NO_2)	

Word	What it means	Picture
locant	the number that says which carbon a group is on	
phenyl	the C ₆ H ₅ – group when the ring is the 'add-on'	
hydrogenation	adding H ₂ to a double bond	

Support pages

My progress tracker

Colour each box: RED = not yet, AMBER = nearly, GREEN = I can do it. Do it again after revision.

I can...	Before	After lesson	After revision
draw benzene two ways and say which is Kekulé			
give the three pieces of evidence for delocalisation			
explain why benzene does not react with bromine water			
name a ring with two groups (lowest numbers, alphabetical)			
write the equation that makes NO_2^+			
draw the 4-move mechanism			
say what a halogen carrier does and write its equations			
give reagents and products for alkylation and acylation			
say how phenol reacts with NaOH , Na_2CO_3 , Br_2 and dilute HNO_3			
explain why phenol is more reactive than benzene			
say where OH , NH_2 and NO_2 send the next group			
plan a two-step synthesis in the right order			