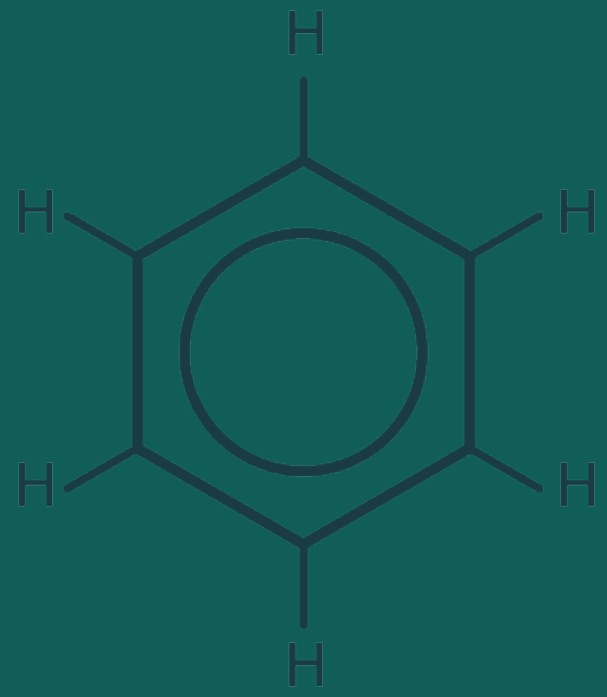
Aromatic Chemistry

Benzene, electrophilic substitution, phenol and directing groups

OCR A Level Chemistry A (H432) — Module 6.1.1



TEACHER COPY — with answers and teaching notes

Colour code: blue = question green = answer amber = key word purple = stretch (beyond the spec)

Based on OCR Chemistry A (Oxford) Chapter 25 and the H432 specification, Module 6.1.1

The journey: 7 lessons

1 — Meet benzene

Kekulé vs delocalised; the evidence

2 — Naming

IUPAC names for substituted rings

3 — Nitration

Electrophilic substitution + mechanism

4 — Halogenation

Halogen carriers; benzene vs alkenes

5 — Friedel–Crafts

Alkylation, acylation, unfamiliar reactions

6 — Phenol

Weak acid; Br_2 and HNO_3; why it's reactive

7 — Directing groups

2,4- vs 3-directing; planning synthesis

Every lesson: Do now → learn with questions → Show me → exit ticket. Purple slides are stretch material for those who want to go beyond the spec.

Lesson 1

1 Meet benzene

TEACHER COPY

Specification 6.1.1 (a) (b) (f) — 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

(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 (from the specification)

- 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.
- HSW2,5: use the delocalised benzene model to explain reactivity.

In plain English — by the end of this lesson I can…

- [ ] describe the Kekulé model and the delocalised model of benzene
- [ ] explain THREE pieces of evidence for the delocalised model
- [ ] explain why benzene does not react with bromine like an alkene does

Do now — retrieval (5 minutes)

Lesson 1

RETRIEVAL 4.1.3 alkenes — recall this first; today builds on it

1

Draw the displayed formula of ethene. What TWO types of bond join the carbon atoms?

Answer

A double bond = one σ (sigma) bond + one π (pi) bond. The π bond is formed by sideways overlap of p-orbitals.

2

What is an electrophile?

Answer

An electron-pair acceptor — a species attracted to a region of high electron density.

3

What do you SEE when bromine water is added to an alkene? What type of reaction is it?

Answer

Orange → colourless. Electrophilic addition.

Benzene: the facts

Lesson 1

SPEC (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

hexane C_6H_{14} vs benzene C_6H_6

Discovered in 1825 by **Michael Faraday**.

A colourless, sweet-smelling, **flammable** liquid.

Found in crude oil, petrol and cigarette smoke.

It is a **carcinogen** — it can cause cancer.

arene / aromatic: a hydrocarbon that contains a benzene ring

Question

Hexane is C_6H_{14}. Benzene is C_6H_6. What does the formula tell you about benzene?

Answer

Benzene has 8 fewer hydrogens than hexane.

It must be very unsaturated (rings and/or multiple bonds).

Chemists expected it to react like an alkene… it does not!

Kekulé's model (1865)

Lesson 1

SPEC (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

Friedrich August Kekulé suggested a **hexagonal** ring of six carbon atoms.

The ring has **alternating** single and double bonds.

Legend says the idea came to him in a daydream about a snake biting its own tail.

Question

If Kekulé were right, benzene would have THREE C=C bonds.
Predict what should happen when bromine water is added.

Answer

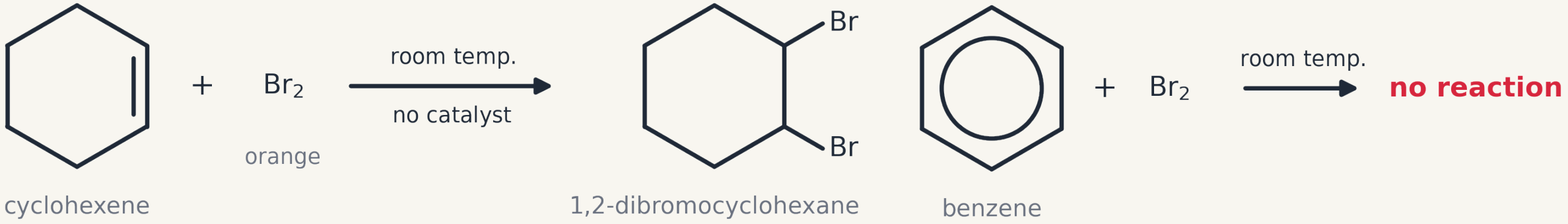
It should decolourise bromine water (orange → colourless).

The reaction would be electrophilic addition — just like an alkene.

Evidence 1: benzene is unreactive

Lesson 1

SPEC (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



Question

Benzene does NOT decolourise bromine water. What does this suggest about the C=C bonds in Kekulé's model?

Answer

Benzene cannot contain normal C=C double bonds.

No electrophilic addition happens — so the model must be wrong (or incomplete).

Evidence 2: bond lengths

Lesson 1

SPEC (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

Kekulé model predicts

X-ray diffraction shows

In 1929 **Kathleen Lonsdale** measured the bonds in benzene using **X-ray diffraction**.

Question

A C–C single bond is 0.153 nm and a C=C double bond is 0.134 nm. What did Lonsdale find, and what does it mean?

Answer

All six bonds are the SAME length: 0.139 nm.

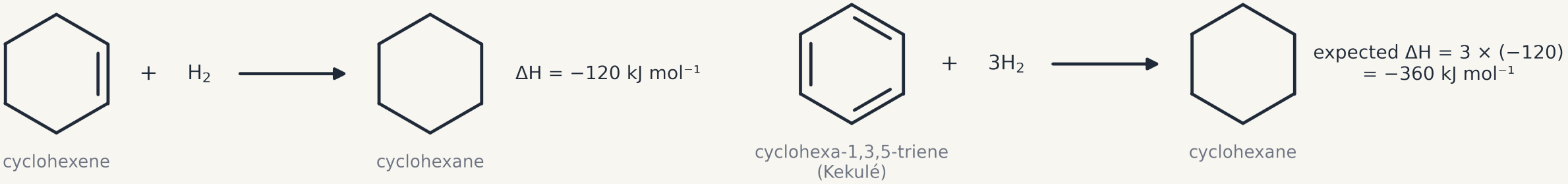
This is between a single and a double bond.

So benzene has NO separate single and double bonds.

Evidence 3: enthalpy change of hydrogenation

Lesson 1

SPEC (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



Hydrogenation = adding H_2 across a C=C bond. Cyclohexene has ONE C=C: ΔH = **−120** kJ mol⁻¹.

hydrogenation: adding hydrogen to an unsaturated compound

Question

Kekulé's benzene (cyclohexa-1,3,5-triene) has THREE C=C bonds. Predict its enthalpy change of hydrogenation.

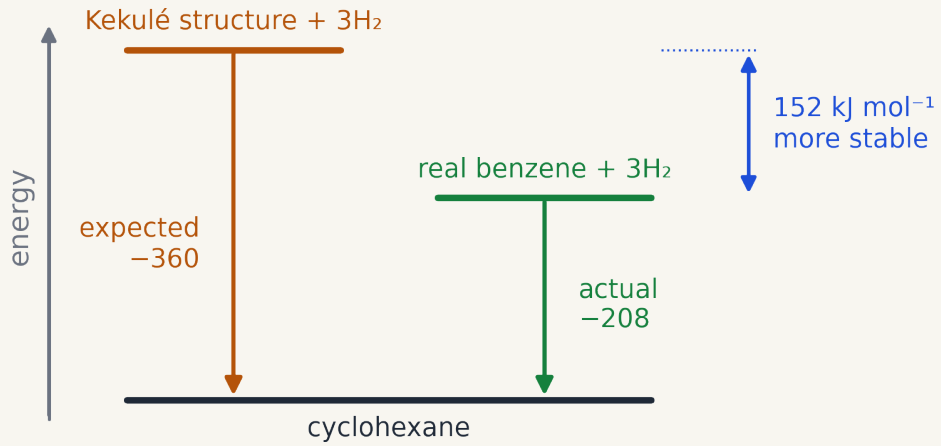
Answer

3 × (−120) = −360 kJ mol⁻¹ (expected).

The real value: benzene is MORE stable

Lesson 1

SPEC (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



Actual ΔH of hydrogenation of benzene = **−208** kJ mol⁻¹.

Question

Work out the difference between the expected and actual values. Is real benzene MORE or LESS stable than Kekulé's structure?

Answer

360 − 208 = 152 kJ mol⁻¹ LESS energy is released than expected.

So real benzene is 152 kJ mol⁻¹ LOWER in energy → MORE stable.

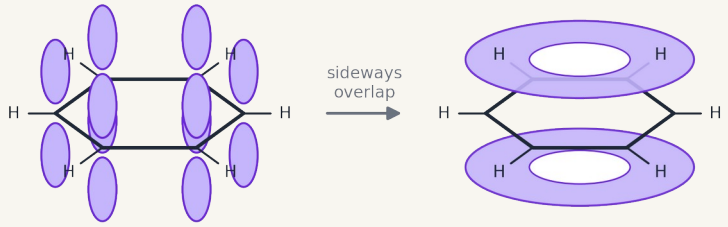
Something extra is stabilising benzene: delocalisation.

delocalisation energy: the **152** kJ mol⁻¹ by which benzene is more stable than Kekulé predicts

The delocalised model

Lesson 1

SPEC (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



one p-orbital on each carbon, at right angles to the ring

rings of electron density above and below the plane

Each carbon uses 3 of its 4 outer electrons in σ bonds (two to carbons, one to hydrogen).

The 4th electron sits in a **p-orbital** at right angles to the ring.

delocalised: electrons that are shared over more than two atoms, not fixed in one bond

Question

What happens when the six neighbouring p-orbitals overlap sideways?

Answer

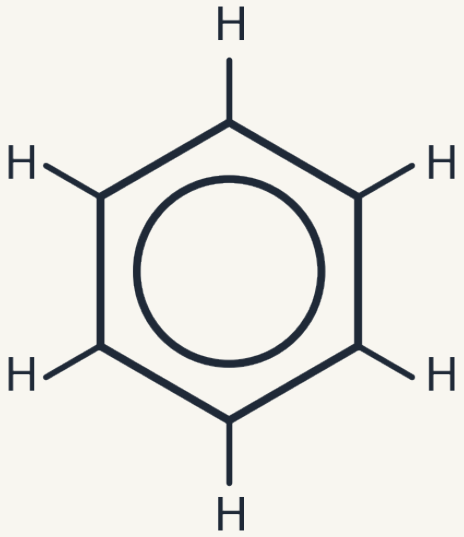
They form a π-system: two rings of electron density above and below the ring.

All 6 electrons are spread over ALL six carbons — delocalised.

Delocalised benzene: the key facts

Lesson 1

SPEC (a)(b) (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



1. Planar (flat) **hexagonal** ring — bond angles **120**°.
2. All C–C bonds the same length: **0.139** nm.
3. Six **delocalised** π electrons above and below the ring.
4. Very **stable**: 152 kJ mol^{-1} more stable than Kekulé predicts.

Question

Match each piece of evidence (reactivity, bond lengths, hydrogenation) to the fact it supports.

Answer

Bond lengths → fact 2.

Hydrogenation → fact 4.

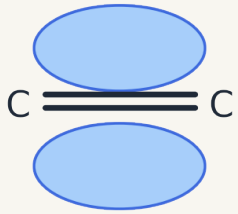
No reaction with Br_2 → facts 3 and 4 (no localised C=C bonds to attack).

Why won't benzene react with bromine? (spec f)

Lesson 1

SPEC (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

localised π bond
= HIGH electron density

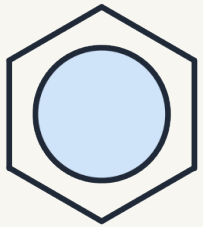


δ+ δ−
Br—Br

dipole induced → electrophile

alkene: reacts (electrophilic addition)

delocalised π system
= LOWER electron density
between any two carbons



Br—Br

no dipole induced → no electrophile

benzene: no reaction without a halogen carrier

Question

Use the words localised, delocalised, electron density and polarise to explain why cyclohexene reacts with Br_2 but benzene does not.

polarise: to induce a dipole (δ+ / δ−) in a molecule

Answer

1. An alkene's π bond is LOCALISED between two carbons → high electron density.
2. This POLARISES Br_2 (induces a dipole, Br δ+) → Br_2 becomes an electrophile → addition.
3. Benzene's π electrons are DELOCALISED over six carbons → lower electron density → cannot polarise Br_2 → no reaction.

Now: your turn — Worksheet 1

Lesson 1

YOUR TURN Practise it now — (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

N O W

Worksheet 1

Core questions 1–6

20 minutes

1. **Core** questions 1–6
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U1 Aromaticity: why 4n + 2? (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Show me (mini-whiteboards)

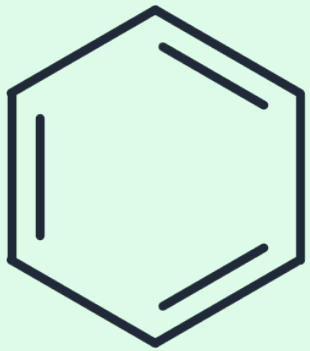
Lesson 1

SPEC (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

Question

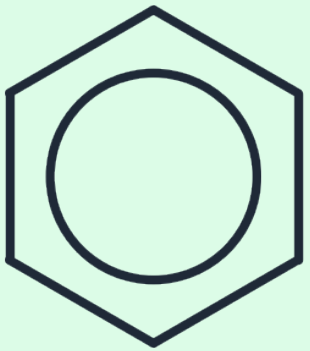
SHOW ME: draw benzene in TWO ways on your whiteboard. Label which one is Kekulé's structure.

Answer



Kekulé structure

or



delocalised structure

Exit ticket

Lesson 1

SPEC CHECK (a)(b)(f) (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 · (f) why benzene resists bromination compared with alkenes: delocalised vs localised π electron density

1 [2 marks]

State the C–C bond length in benzene and explain what it tells us.

Answer

All 0.139 nm; between a single (0.153 nm) and a double bond (0.134 nm) → no alternating single/double bonds.

2 [3 marks]

Explain why the enthalpy change of hydrogenation of benzene is evidence for delocalisation.

Answer

Kekulé structure (3 C=C) predicts 3 × (−120) = −360 kJ mol^{-1}; actual is −208 kJ mol^{-1}; 152 kJ mol^{-1} less exothermic → benzene more stable than expected → electrons delocalised.

3 [2 marks]

Why does benzene not decolourise bromine water?

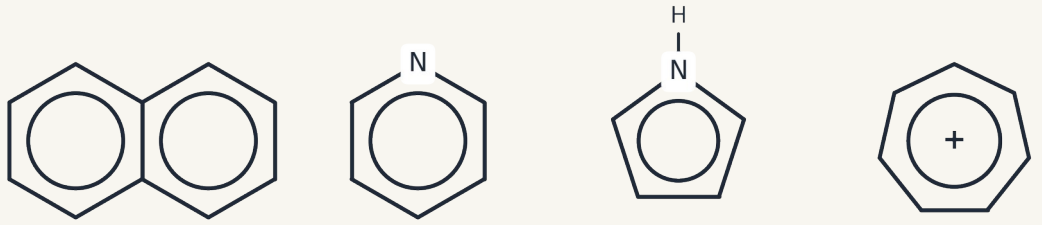
Answer

π electrons are delocalised → lower electron density between carbons → cannot polarise / induce a dipole in Br_2 → no electrophile forms.

STRETCH: what makes a ring aromatic?

Lesson 1

BEYOND THE SPEC Extension — not examined. see Stretch Pack §1



naphthalene pyridine pyrrole tropylium cation

Hückel's rule: a planar, fully conjugated ring is aromatic if it has (4n + 2) π electrons (n = 0, 1, 2 …).

Benzene: 6 π electrons → n = 1 ✓

Stretch

Cyclooctatetraene, C_8H_8, is a ring with four C=C bonds. Is it aromatic? What about naphthalene (two fused rings, 10 π electrons) and pyridine?

Answer

C_8H_8: 8 π electrons = 4n, not 4n + 2 → NOT aromatic; it is tub-shaped, not planar, and reacts like an alkene.

Naphthalene: 10 = 4(2) + 2 → aromatic. Pyridine: 6 (the N lone pair is NOT in the ring) → aromatic.

Pyrrole: aromatic — its N lone pair IS part of the ring, making 6.

Lesson 2

2 Naming aromatic compounds

TEACHER COPY

Specification 6.1.1 (c) — 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 (from the specification)

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

In plain English — by the end of this lesson I can…

- [ ] name compounds with ONE group on the ring
- [ ] use 'phenyl' when the ring is the add-on
- [ ] number the ring to name compounds with TWO or more groups

Do now — retrieval (5 minutes)

Lesson 2

RETRIEVAL 4.1.1 nomenclature — recall this first; today builds on it

1

Name $CH_3CHClCH_3$.

Answer

2-chloropropane

2

Name $CH_3CH(OH)CH_3$.

Answer

propan-2-ol

3

What is the empirical formula of benzene, C_6H_6?

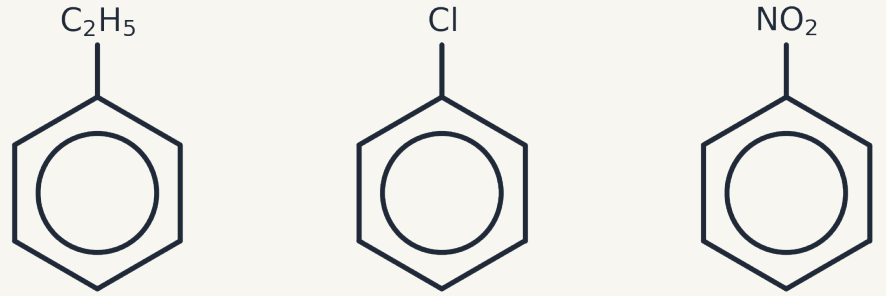
Answer

CH

Rule 1: one group — prefix + benzene

Lesson 2

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



ethylbenzene chlorobenzene nitrobenzene

Short alkyl groups (CH_3, C_2H_5), halogens (F, Cl, Br, I) and the nitro group (NO_2) are written as **prefixes** in front of 'benzene'.

Question

Name the three compounds shown.

Answer

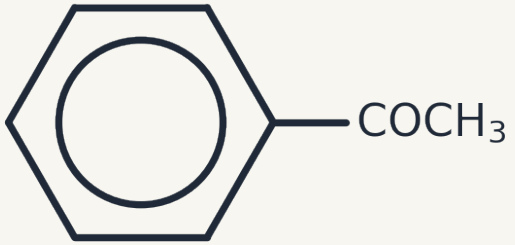
ethylbenzene, chlorobenzene, nitrobenzene.

($C_6H_5CH_3$ is methylbenzene.)

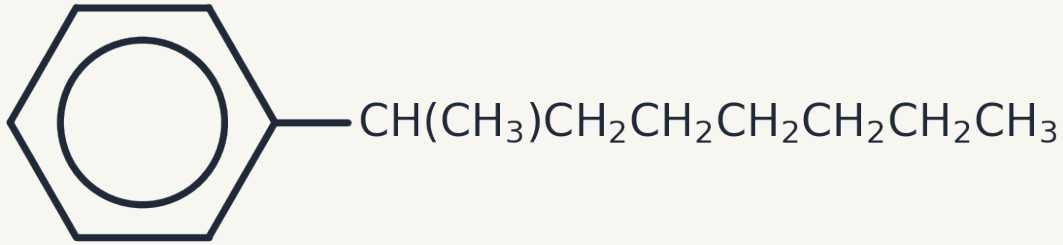
Rule 2: when the ring is the add-on — 'phenyl'

Lesson 2

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



phenylethanone



2-phenyloctane

If the ring is attached to a chain with a **functional group**, or to a chain of **7** or more carbons, the ring becomes a substituent called **phenyl** (C_6H_5–).

phenyl: the C_6H_5– group, used when benzene is a substituent

Question

Why is $C_6H_5COCH_3$ called phenylethanone, not 'ethanoylbenzene'?

Answer

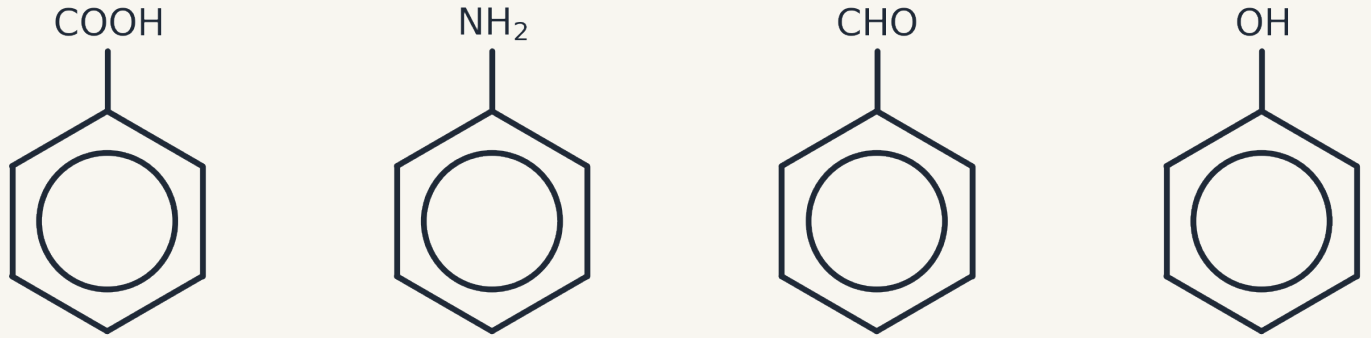
The ketone (C=O) is the main functional group, so the two-carbon chain 'ethanone' is the parent.

The ring is named as a phenyl substituent on carbon 1 of the chain.

Rule 3: four names to LEARN

Lesson 2

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



benzoic acid | phenylamine | benzaldehyde | phenol

Some names do not follow the rules — you just have to know them.

Question

Name A–D. Which one would fizz with sodium carbonate? Which one is a base?

Answer

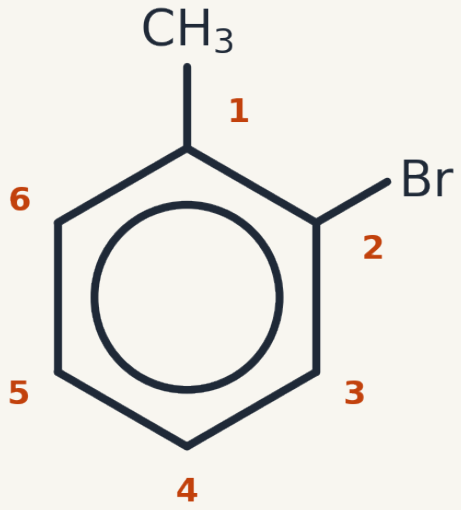
A benzoic acid (C_6H_5COOH); B phenylamine ($C_6H_5NH_2$); C benzaldehyde (C_6H_5CHO); D phenol (C_6H_5OH).

Benzoic acid fizzes with Na_2CO_3 (–COOH). Phenylamine is a base (–NH_2, like ammonia).

Rule 4: two or more groups — number the ring

Lesson 2

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



Step 1: choose the parent (e.g. methylbenzene → the CH_3 carbon is carbon **1**).

Step 2: number round the ring so the groups get the **lowest** possible numbers.

Step 3: write prefixes in **alphabetical** order.

Question

Why is this compound called 2-bromomethylbenzene and NOT 6-bromomethylbenzene?

Answer

You can number clockwise or anticlockwise.

Choose the direction that gives the LOWEST number: 2 is lower than 6.

Now: your turn — Worksheet 2

Lesson 2

YOUR TURN Practise it now — (c) IUPAC rules for naming substituted aromatic compounds

N O W

Worksheet 2

Core questions 1–3

12 minutes

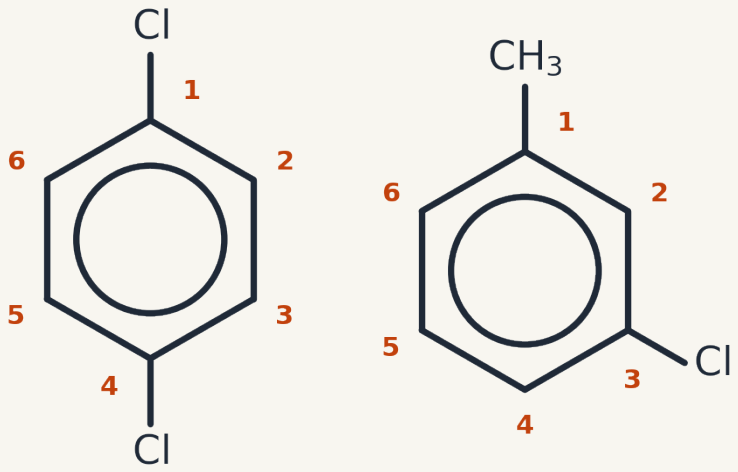
1 **Core** questions 1–3

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Worked examples

Lesson 2

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



Question

Name each compound. Check: lowest numbers? Alphabetical order?

Answer

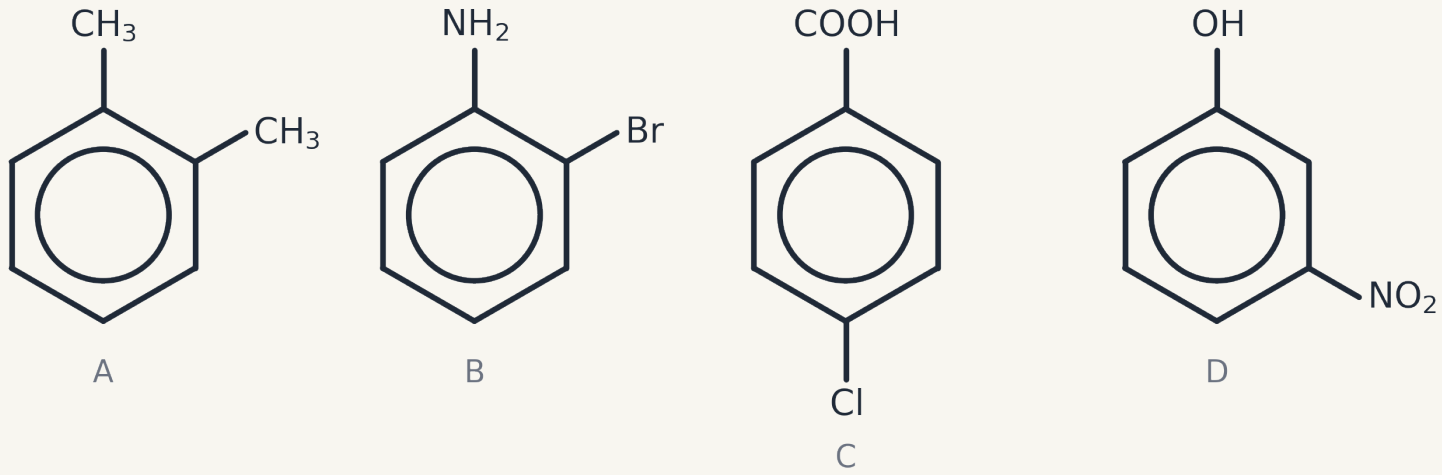
Left: 1,4-dichlorobenzene — two identical groups → 'di', and BOTH are numbered.

Right: 3-chloromethylbenzene — methylbenzene is the parent, so the CH_3 carbon is C1.

Your turn: name these

Lesson 2

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



Question

Name compounds A–D.

Answer

A: 1,2-dimethylbenzene

B: 2-bromophenylamine

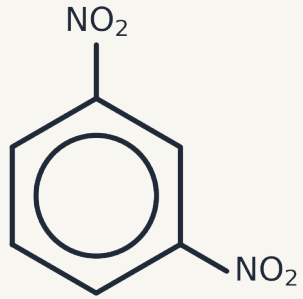
C: 4-chlorobenzoic acid

D: 3-nitrophenol

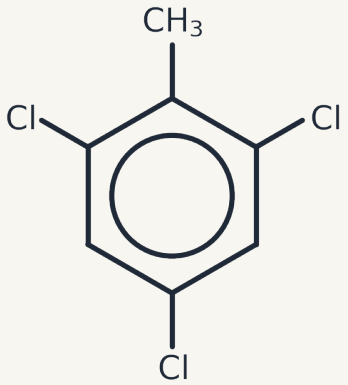
Your turn: draw these

Lesson 2

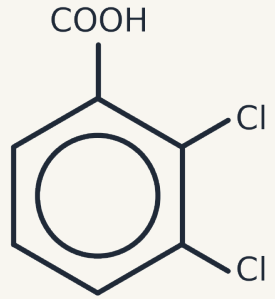
SPEC (c) use of IUPAC rules of nomenclature for systematically naming substituted aromatic compounds



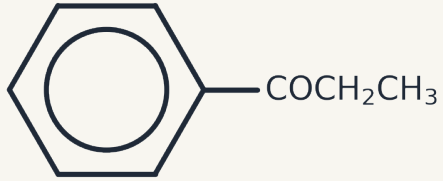
(a) 1,3-dinitrobenzene



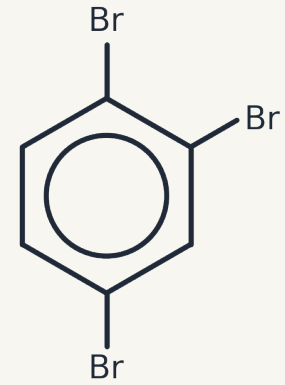
(b) 2,4,6-trichloro-methylbenzene



(c) 2,3-dichloro-benzoic acid



(d) phenylpropanone



(e) 1,2,4-tribromobenzene

Question

Draw the skeletal formula of: (a) 1,3-dinitrobenzene (b) 2,4,6-trichloromethylbenzene (c) 2,3-dichlorobenzoic acid (d) phenylpropanone (e) 1,2,4-tribromobenzene

Answer

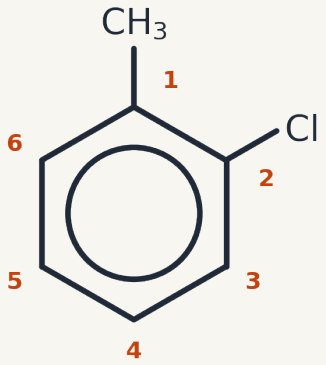
(a) NO_2 on carbons 1 and 3. (b) CH_3 on C1, Cl on C2, C4 and C6.

(c) COOH on C1, Cl on C2 and C3. (d) $C_6H_5COCH_2CH_3$. (e) Br on C1, C2 and C4.

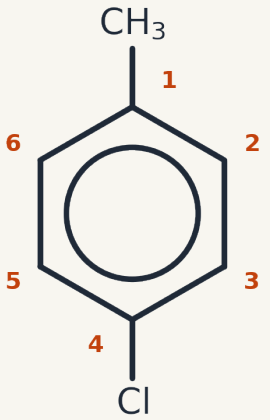
Spot the mistake

Lesson 2

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



Student's drawing of '4-chloromethylbenzene'



?

Question

A student drew '4-chloromethylbenzene' as the LEFT structure. What is wrong? Which structure is correct?

Answer

In the left structure the Cl is on carbon 2 → that is 2-chloromethylbenzene.

In 4-chloromethylbenzene the Cl is OPPOSITE the CH_3 (carbon 4) — the right-hand structure.

Now: your turn — Worksheet 2

Lesson 2

YOUR TURN Practise it now — (c) IUPAC rules for naming substituted aromatic compounds

NOW

Worksheet 2

Core questions 4–6

10 minutes

1. **Core** questions 4–6
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H3 — same ideas, more to think about
4. **Finished those?** Uni worksheet U2 ortho, meta, para and trivial names (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Exit ticket

Lesson 2

SPEC CHECK (c) (c) IUPAC rules for naming substituted aromatic compounds

1 [1 mark]

Name $C_6H_5CH_2CH_3$.

Answer

ethylbenzene

2 [1 mark]

Draw 2,4-dinitromethylbenzene.

Answer

CH_3 on C1; NO_2 on C2 and C4.

3 [1 mark]

A compound has a benzene ring with –OH on carbon 1 and –Cl on carbons 2 and 4. Give its systematic name.

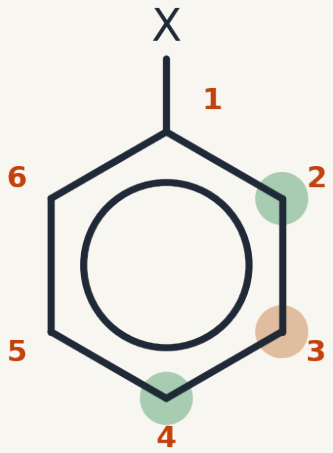
Answer

2,4-dichlorophenol

STRETCH: ortho, meta and para

Lesson 2

BEYOND THE SPEC Extension — not examined. (used in 25.4 of the textbook)



position 2 (and 6) = ortho

position 3 (and 5) = meta

position 4 = para

University textbooks (and older papers) use ortho (o-), meta (m-) and para (p-) for positions 2, 3 and 4 relative to the first group.

Trivial names you will meet: toluene = methylbenzene; aniline = phenylamine; xylene = dimethylbenzene.

Stretch

Give the o/m/p name AND the IUPAC name for 1,4-dichlorobenzene and for 3-nitrophenol. Why can't o/m/p be used for a ring with THREE groups?

Answer

p-dichlorobenzene = 1,4-dichlorobenzene; m-nitrophenol = 3-nitrophenol.

o/m/p only describes the relationship between TWO groups — with three, it becomes ambiguous, so locants are needed.

Lesson 3

TEACHER COPY

3 Electrophilic substitution: nitration

Specification 6.1.1 (d)(i) (e) — 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 (from the specification)

• 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.

In plain English — by the end of this lesson I can…

- ☐ write the equation and conditions for the nitration of benzene
- ☐ write the equation for making the electrophile, NO_2^+
- ☐ draw the full mechanism with curly arrows and explain the role of the catalyst

Do now — retrieval (5 minutes)

Lesson 3

RETRIEVAL 4.1.1 (h)(i) mechanisms — recall this first; today builds on it

1

Define 'electrophile'.

Answer

An electron-pair acceptor.

2

What does a curly arrow show?

Answer

The movement of a PAIR of electrons (from where the pair is, to where it ends up).

3

Why does benzene not undergo addition reactions easily?

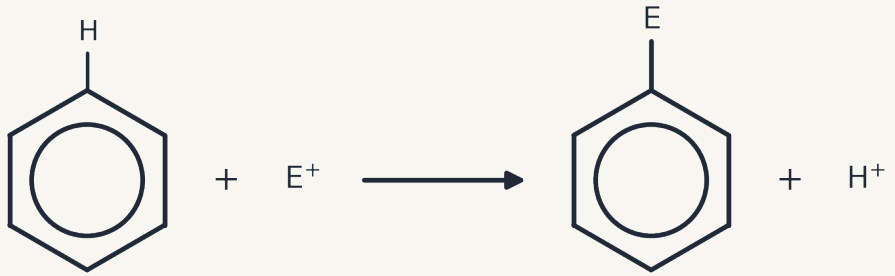
Answer

Addition would destroy the stable delocalised π-system (losing about 152 kJ mol^{-1} of stability).

Substitution — not addition

Lesson 3

SPEC (d) the electrophilic substitution of aromatic compounds with (i) concentrated nitric acid in the presence of concentrated sulfuric acid, (ii) a halogen in the presence of a halogen carrier, (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction)



Benzene reacts with electrophiles, E^+.

A hydrogen atom on the ring is **replaced** by the electrophile.

The stable delocalised ring is **kept**.

electrophilic substitution: an electrophile replaces an atom (H) on the ring

Question

Why does benzene 'prefer' substitution to addition?

Answer

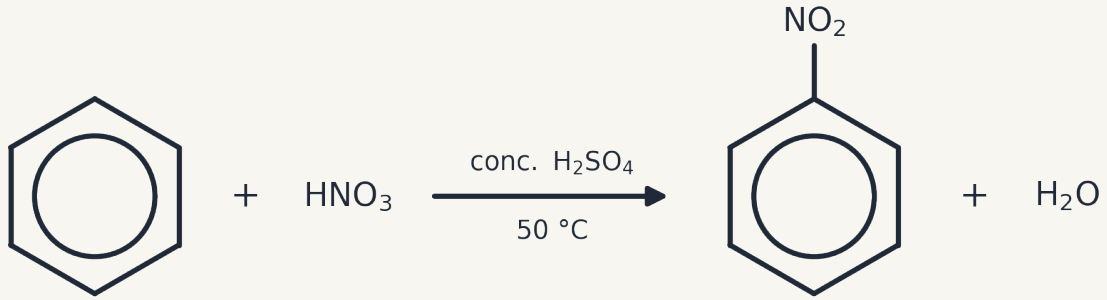
Addition would break up the delocalised π-system and lose the 152 kJ mol^{-1} of extra stability.

Substitution swaps an H for E and keeps the delocalised ring intact.

Nitration: the overall reaction

Lesson 3

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



Reagents: **conc. nitric acid** + **conc. sulfuric acid** (catalyst). Conditions: **50** °C, water bath.

nitration: replacing H with a nitro group, $–NO_2$

Question

Why must the temperature be kept at 50 °C and not higher?

Answer

Above 50 °C further substitution occurs → 1,3-dinitrobenzene forms (impure product).

A water bath keeps the temperature steady so the rate is controlled.

Step 1: making the electrophile

Lesson 3

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

The electrophile is NOT nitric acid. It is the nitronium ion, **NO_2^+**.

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

Question

Which acid is acting as the ACID (proton donor) in Step 1? So what is HNO_3 acting as?

nitronium ion: NO_2^+ — the electrophile in nitration

Answer

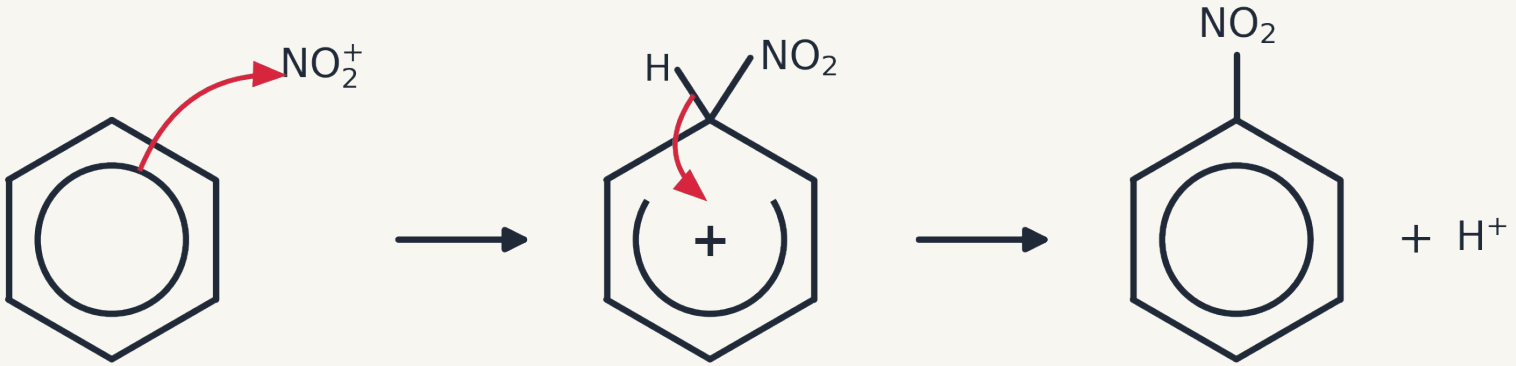
H_2SO_4 is the stronger acid: it donates a proton (H^+) to HNO_3.

So HNO_3 acts as a BASE here. The protonated nitric acid, $H_2NO_3^+$, loses water to give NO_2^+.

Step 2: the mechanism

Lesson 3

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



benzene intermediate

1. An electron pair from the ring forms a bond to the N of NO_2^+.
2. Intermediate: positive charge; the 'horseshoe' shows delocalisation is partly broken.
3. The C–H bond breaks; its electrons return to the ring. The ring re-forms and H^+ leaves.

Question

Where must the FIRST curly arrow start, and where must it finish?

Answer

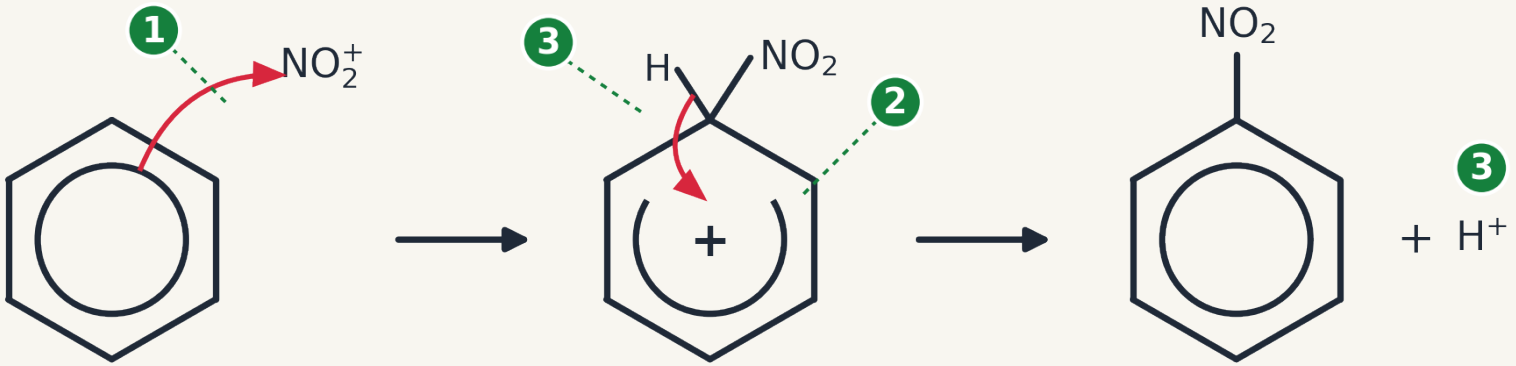
Start: on the delocalised π-ring (the circle) — that is where the electron pair comes from.

Finish: on the N atom of NO_2^+ — the atom carrying the positive charge.

Where the 3 marks are

Lesson 3

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



benzene intermediate

① Arrow 1: tail **on the circle** (the electron pair), head **touching** the N of NO_2^+ — never an O.

② Intermediate: **horseshoe** stopping either side of the carbon that holds the H and NO_2; + **inside** it; H and NO_2 on the **same carbon**.

③ Arrow 2: tail on the **middle of the C–H bond** (never the H), head **into the ring** towards the +. Products: nitrobenzene + H^+.

Question

A 'show the role of the catalyst' mechanism question is worth 5 marks. Where are the other two?

Answer

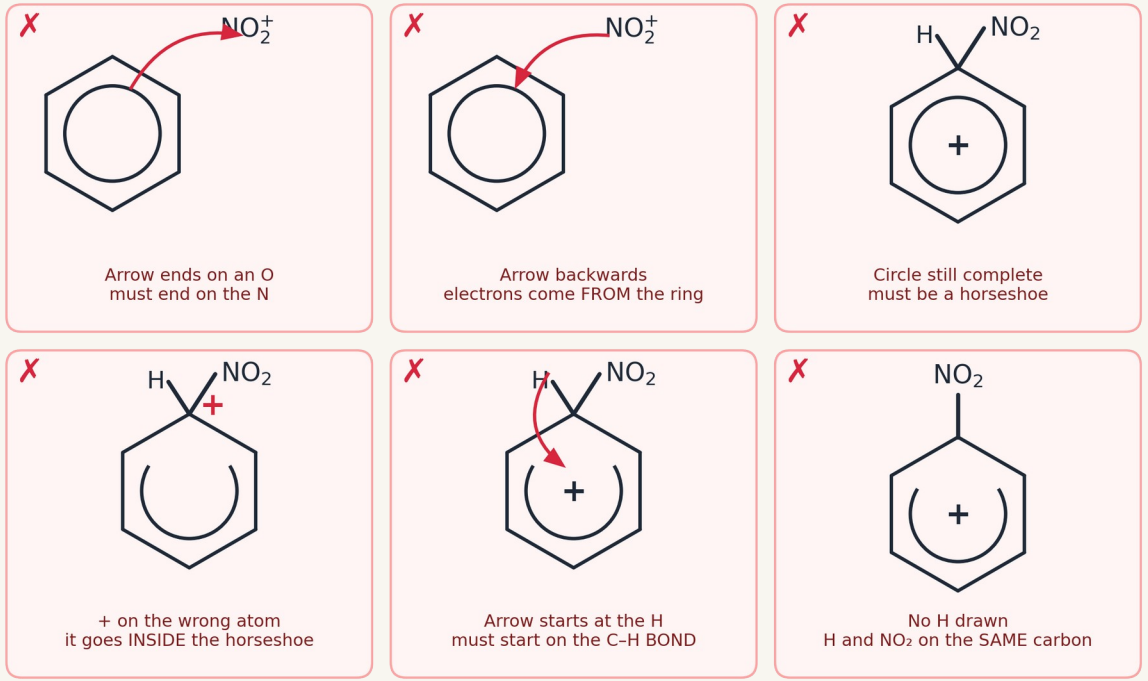
Making the electrophile: $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

Regenerating the catalyst: $H^+ + HSO_4^- \rightarrow H_2SO_4$

Six ways to lose the mark

Lesson 3

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



Question

Each drawing loses ONE of the three marks. Say which mark (1, 2 or 3) — and what the fix is.

Answer

Top row: mark 1 (head must touch the N) · mark 1 (electrons come FROM the ring) · mark 2 (horseshoe, not a circle).

Bottom row: mark 2 (+ inside the horseshoe) · mark 3 (tail on the C–H BOND) · mark 2 (H and NO_2 on the same carbon).

Now: your turn — Worksheet 3

Lesson 3

YOUR TURN Practise it now — (e) the mechanism of electrophilic substitution for nitration and halogenation

N O W

Worksheet 3

Core questions 1–4: mechanism, marks table, checklist

12 minutes

1 **Core** questions 1–4: mechanism, marks table, checklist

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Step 3: regenerating the catalyst

Lesson 3

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

$H^+ + HSO_4^- \rightarrow H_2SO_4$

Question

Use Step 1 and Step 3 to explain why H_2SO_4 is a catalyst.

catalyst: speeds up a reaction and is regenerated — not used up overall

Answer

It is used up in Step 1 (it protonates HNO_3 to make NO_2^+) …

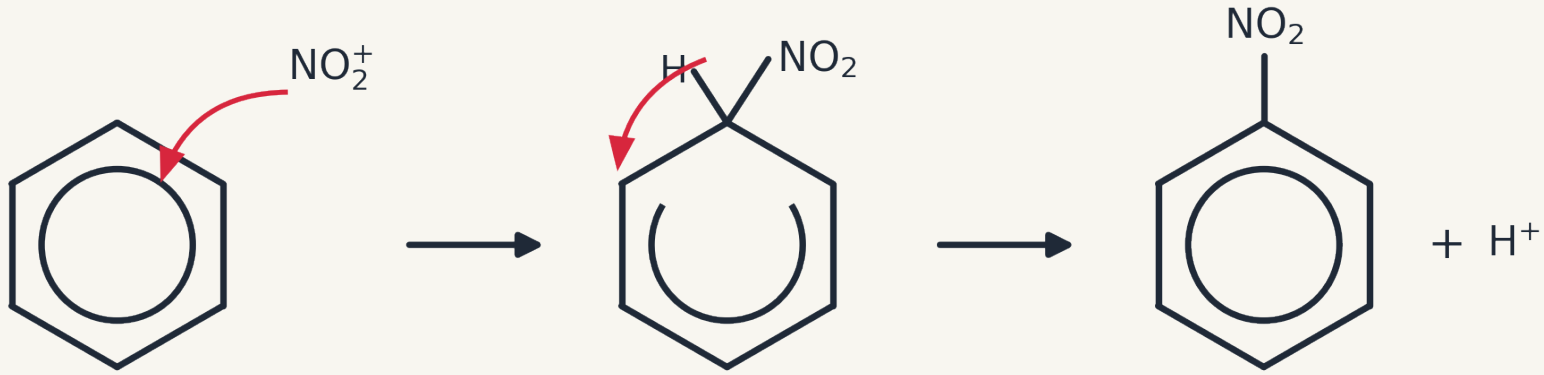
… and regenerated in Step 3, so it is not used up overall.

It provides an alternative route (via NO_2^+) with a lower activation energy.

Exam skills: mark this mechanism

Lesson 3

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



Question

This student's mechanism has THREE mistakes. Find them and say how to fix each one.

Answer

1. The first arrow points the wrong way — it must start at the ring (electron pair) and go TO the N of NO_2^+.
2. The intermediate is missing its + charge.
3. The second arrow must start on the C–H BOND (not the H atom) and go into the ring.

Now: your turn — Worksheet 3

Lesson 3

YOUR TURN Practise it now — (e) the mechanism of electrophilic substitution for nitration and halogenation

NOW

Worksheet 3

Core questions 5–8

12 minutes

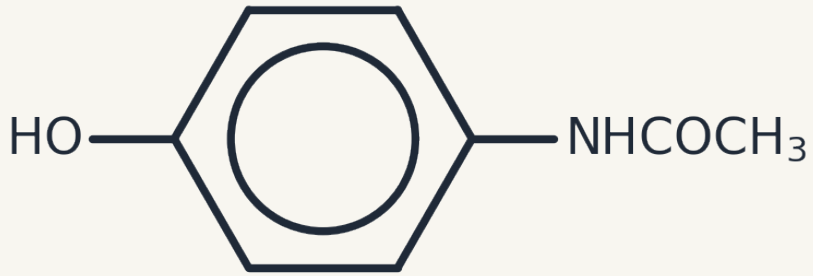
1. **Core** questions 5–8
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U3 The Wheland intermediate (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Why bother nitrating benzene?

Lesson 3

SPEC (d) the electrophilic substitution of aromatic compounds with (i) concentrated nitric acid in the presence of concentrated sulfuric acid, (ii) a halogen in the presence of a halogen carrier, (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction)



paracetamol

Nitrobenzene is a starting material for dyes, pesticides and medicines such as **paracetamol**.

The $–NO_2$ group can later be reduced to $–NH_2$ (Module 6.2.1).

Question

Paracetamol has an –OH and an $–NHCOCH_3$ group on the ring. Are they 1,2- , 1,3- or 1,4- to each other?

Answer

1,4- (opposite each other) — 'para'.

Exit ticket

Lesson 3

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

1 [1 mark]

Write the equation for the formation of the nitronium ion.

Answer

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

2 [3 marks]

Draw the mechanism for the nitration of benzene, including the intermediate.

Answer

Arrow from ring to N of NO_2^+; intermediate with horseshoe and + charge, H and NO_2 on the same carbon; arrow from C–H bond into ring; nitrobenzene + H^+.

3 [2 marks]

State the conditions for nitration and explain the role of H_2SO_4.

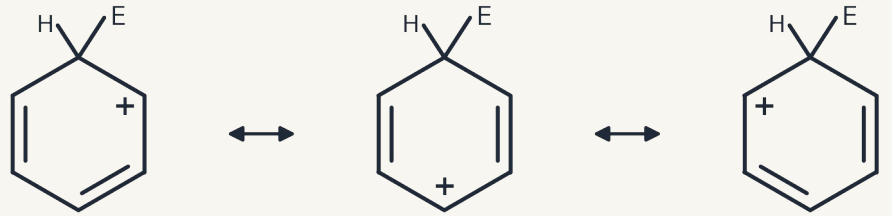
Answer

Conc. HNO_3 + conc. H_2SO_4, 50 °C (water bath). H_2SO_4 is a catalyst: makes NO_2^+ (step 1) and is regenerated by $H^+ + HSO_4^- \rightarrow H_2SO_4$ (step 3).

STRETCH: why can the intermediate exist at all?

Lesson 3

BEYOND THE SPEC Extension — not examined. Stretch Pack §3



the positive charge is shared over three carbons (positions 2, 4 and 6 relative to the attacked carbon)

The intermediate (the 'Wheland intermediate' or arenium ion) keeps 4 π electrons over 5 carbons. The + charge is shared, not stuck on one atom.

Stretch

Which carbons carry the positive charge, relative to the attacked carbon? Why is step 2 (attack) slow but step 3 (loss of H^+) fast?

Answer

Positions 2, 4 and 6 (ortho and para to the attacked carbon) — three resonance forms.

Step 2 breaks aromaticity → high activation energy → rate-determining. Step 3 restores aromaticity → very favourable and fast.

Evidence: nitration shows no kinetic isotope effect (C–D reacts as fast as C–H), so C–H cleavage is not in the slow step.

Lesson 4

TEACHER COPY

4 Halogenation and halogen carriers

Specification 6.1.1 (d)(ii) (e) (f) — 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 (from the specification)

- 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.

In plain English — by the end of this lesson I can…

- [ ] write equations for the bromination and chlorination of benzene
- [ ] draw the mechanism, including making the electrophile and regenerating the catalyst
- [ ] compare the reactions of benzene and alkenes with bromine

Do now — retrieval (5 minutes)

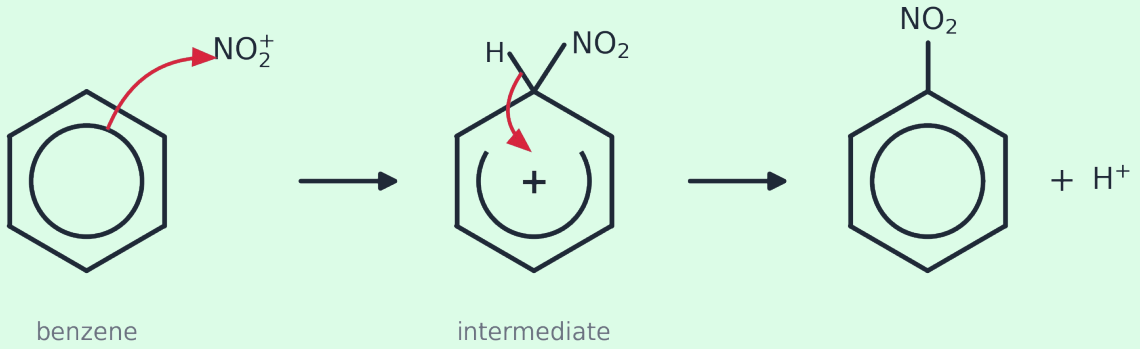
Lesson 4

RETRIEVAL Lesson 3 — recall this first; today builds on it

1

Complete the nitration mechanism on your copy: add the curly arrows, the + charge and the products.

Answer



2

Write the equation for the formation of NO_2^+.

Answer

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

3

What does 'delocalised' mean?

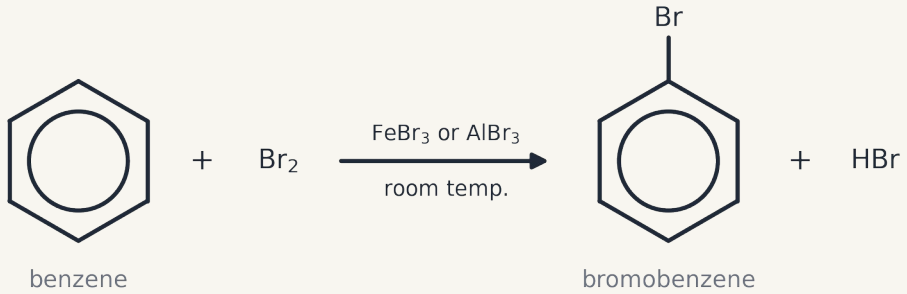
Answer

Electrons spread over several atoms (all six carbons), not fixed in one bond.

Bromination: the overall reaction

Lesson 4

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



Benzene reacts with bromine ONLY if a **halogen carrier** catalyst is present: $FeBr_3$, $AlBr_3$, $AlCl_3$, $FeCl_3$ or **iron** filings (which make $FeBr_3$ in situ).

Conditions: room temperature and pressure.

halogen carrier: a catalyst (Fe, $FeBr_3$, $AlCl_3$ …) that generates the halogen electrophile

Question

Cyclohexene needs no catalyst but benzene does. Why? (Look back at Lesson 1.)

Answer

Benzene's delocalised π electrons cannot polarise Br_2.

The halogen carrier makes a much stronger electrophile, Br^+, which CAN attack the ring.

Step 1: making the electrophile

Lesson 4

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

$Br_2 + FeBr_3 \rightarrow FeBr_4^- + Br^+$

Br^+ is called the **bromonium** ion. (The spec lets you assume the electrophile is X^+.)

Question

What is $FeBr_3$ doing to the Br_2 molecule? Think about electron pairs.

Answer

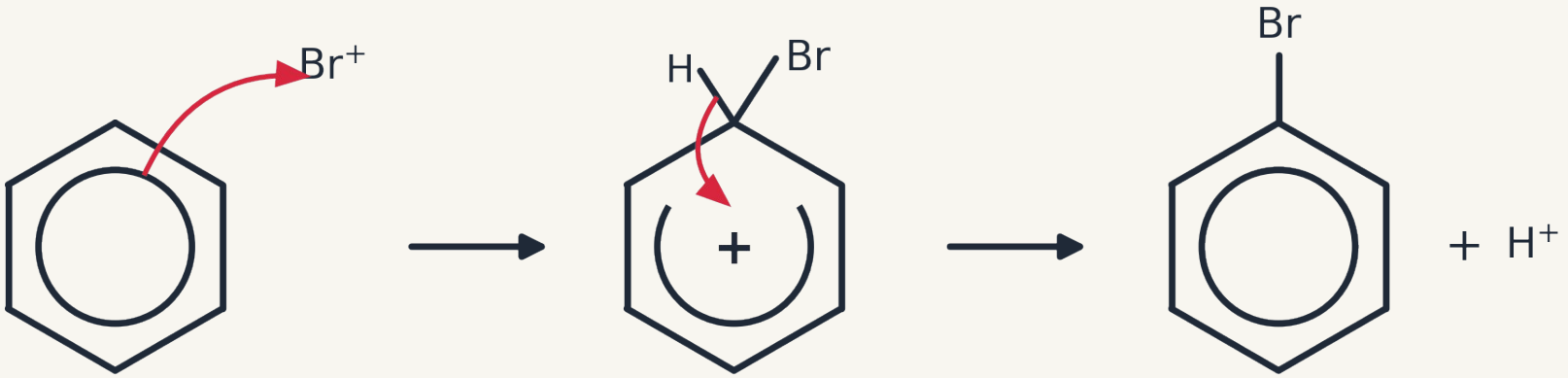
$FeBr_3$ accepts a bromide ion, Br^-, together with its bonding pair of electrons, from Br_2.

This leaves Br^+ — a powerful electrophile. $FeBr_3$ is an electron-pair acceptor (a Lewis acid — see the stretch).

Step 2: the mechanism — same pattern!

Lesson 4

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



benzene intermediate

Question

Compare this with nitration. What is the SAME? What is DIFFERENT?

Answer

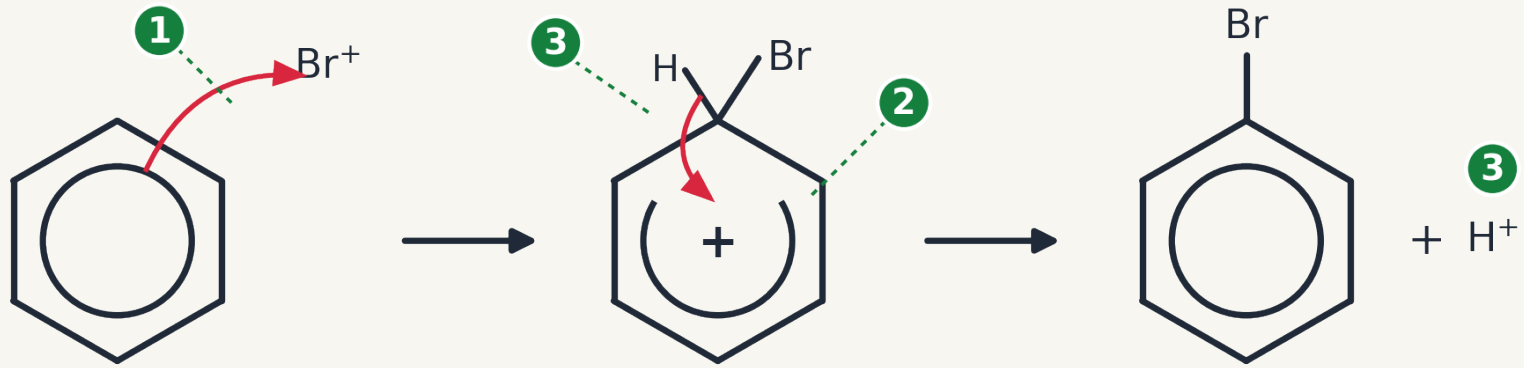
Same: arrow from ring to E^+; horseshoe intermediate with +; C–H bond electrons return to the ring; H^+ leaves.

Different: the electrophile is Br^+ (not NO_2^+); the product is bromobenzene; H^+ is mopped up by $FeBr_4^-$ giving HBr.

Same 3 marks — with Br^+

Lesson 4

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



benzene intermediate

① Arrow 1: tail **on the circle** (the electron pair), head **touching** Br^+.

② Intermediate: **horseshoe** stopping either side of the carbon that holds the H and Br; + **inside** it; H and Br on the **same carbon**.

③ Arrow 2: tail on the **middle of the C–H bond** (never the H), head **into the ring** towards the +. Products: bromobenzene + H^+.

Question

Two more marks are on offer in a halogenation question. Write the two equations that earn them.

Answer

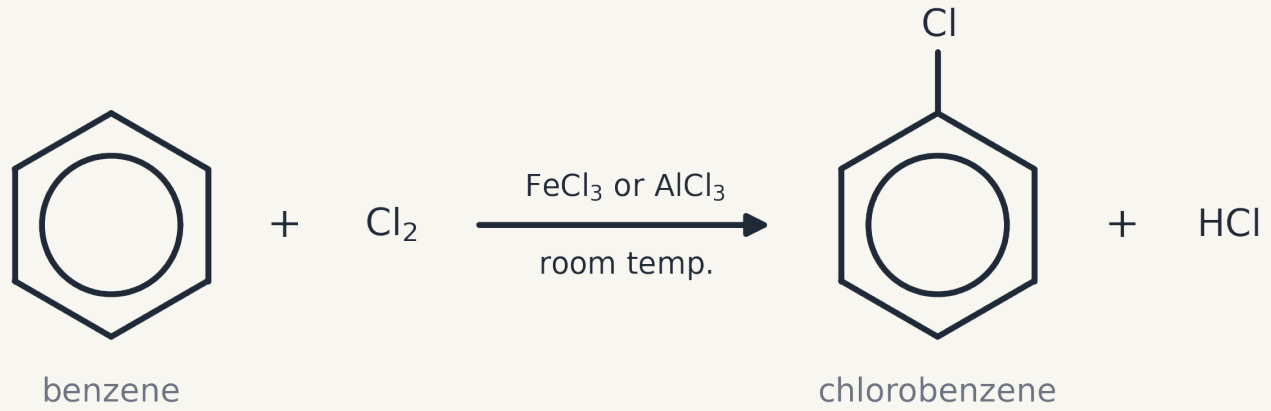
Making the electrophile: $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$

Regenerating the catalyst: $H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$

Step 3: regenerating the catalyst

Lesson 4

SPEC (d(ii))(e) (d(ii)) electrophilic substitution with a halogen + a halogen carrier · (e) the mechanism of electrophilic substitution for nitration and halogenation



$H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$

Question

Chlorine reacts the same way with an $AlCl_3$ catalyst. Write ALL THREE steps for the chlorination of benzene.

Answer

Step 1: $Cl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl^+$

Step 2: benzene + Cl^+ → intermediate → chlorobenzene + H^+ (same mechanism)

Step 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Now: your turn — Worksheet 4

Lesson 4

YOUR TURN Practise it now — (d(ii)) electrophilic substitution with a halogen + a halogen carrier · (e) the mechanism of electrophilic substitution for nitration and halogenation

N O W

Worksheet 4

Core questions 1–4

12 minutes

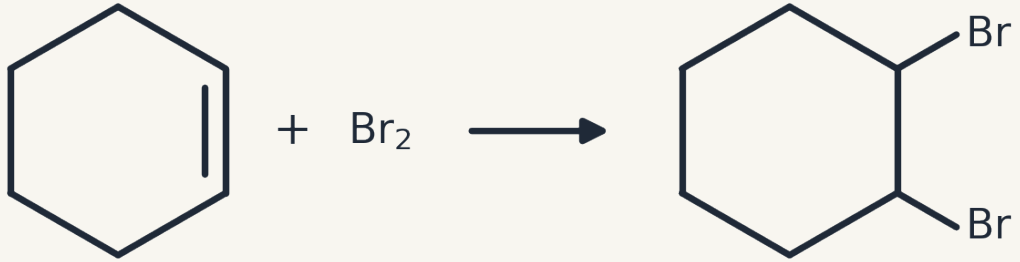
1 **Core** questions 1–4

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

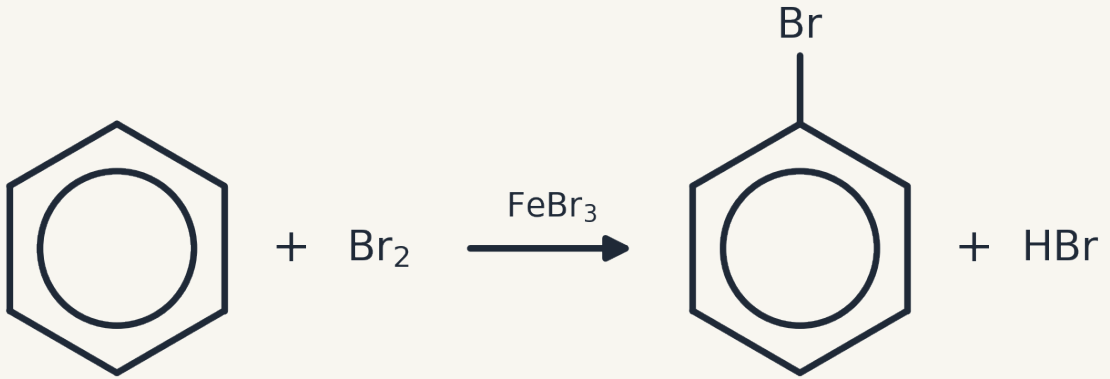
Alkene vs arene with bromine

Lesson 4

SPEC (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



electrophilic ADDITION — no catalyst — bromine decolourised



electrophilic SUBSTITUTION — halogen carrier needed

? Question

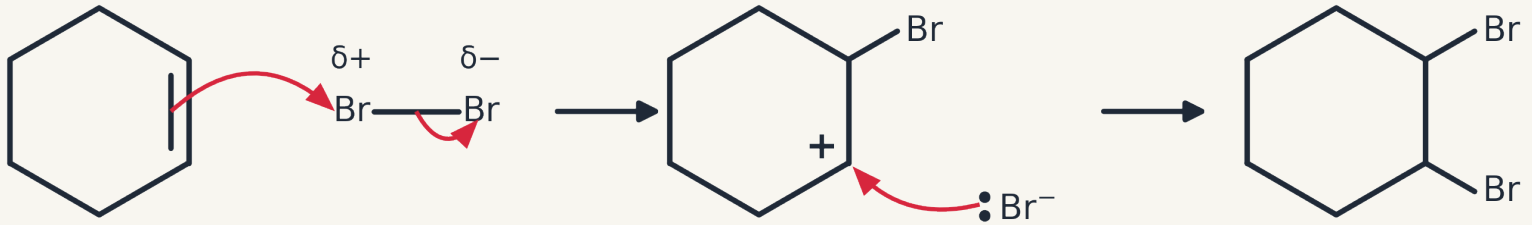
Copy and complete the comparison table.

	Cyclohexene	Benzene
Type of reaction	electrophilic addition	**electrophilic substitution**
Catalyst?	none needed	**halogen carrier ($FeBr_3$)**
Observation	orange → colourless	**no change without catalyst; HBr fumes with catalyst**
Product(s)	1,2-dibromocyclohexane	**bromobenzene + HBr**

The 4-mark explanation (spec f)

Lesson 4

SPEC (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



cyclohexene — carbocation intermediate — 1,2-dibromocyclohexane

Alkene arrows (from 4.1.3): 1 from the **C=C π bond** to the δ+ Br · 2 from the **Br–Br bond** to the δ− Br · 3 from the **lone pair on Br⁻** to the C⁺.

Question

Explain why alkenes react with bromine without a catalyst but benzene does not. (4 marks)

Answer

1. Alkene: π electrons LOCALISED between two carbons → high electron density.
2. This POLARISES Br–Br (induced dipole); Br δ+ is the electrophile → addition.
3. Benzene: π electrons DELOCALISED over six carbons → lower electron density.
4. Cannot polarise Br_2 → no electrophile → no reaction (needs a halogen carrier to make Br^+).

Now: your turn — Worksheet 4

Lesson 4

YOUR TURN Practise it now — (f) why benzene resists bromination compared with alkenes: delocalised vs localised π electron density

NOW

Worksheet 4

Core questions 5–6

10 minutes

1. **Core** questions 5–6
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U4 Halogen carriers are Lewis acids (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Show me (mini-whiteboards)

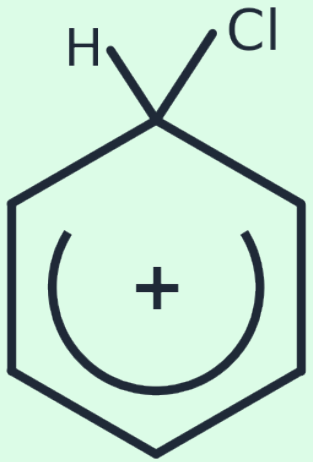
Lesson 4

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

Question

SHOW ME: draw the INTERMEDIATE for the chlorination of benzene. Include the charge.

Answer



Exit ticket

Lesson 4

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

1 [1 mark]

Write an equation to show how the electrophile is formed when Br_2 reacts with $FeBr_3$.

Answer

$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$

2 [4 marks]

Outline the mechanism for the reaction of benzene with chlorine using an $AlCl_3$ catalyst, including how the electrophile is generated.

Answer

$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$; arrow from ring to Cl^+; intermediate with + and horseshoe; arrow from C–H bond to ring; chlorobenzene + H^+; $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$.

3 [3 marks]

Explain why benzene is less reactive with bromine than cyclohexene.

Answer

Benzene's π electrons are delocalised → lower electron density → cannot polarise Br_2 / induce a dipole → no electrophile; alkene has localised π bond with high electron density which polarises Br_2.

STRETCH: halogen carriers are Lewis acids

Lesson 4

BEYOND THE SPEC Extension — not examined. Stretch Pack §5

A Lewis acid is an electron-pair ACCEPTOR; a Lewis base is an electron-pair DONOR.

$AlCl_3$ has only six electrons around Al, and $FeBr_3$ has an empty orbital on Fe — both accept an electron pair from Br_2 or Cl_2.

Stretch

(a) Why does iron metal work as a 'halogen carrier'? (b) Iodination of benzene with I_2/FeI_3 barely works — suggest why. (c) Why is fluorination not done this way?

Answer

(a) $2Fe + 3Br_2 \rightarrow 2FeBr_3$ — the real catalyst is made in situ.

(b) I^+ is a weak electrophile; the reaction is endothermic/reversible (the HI formed reduces the product back), so an oxidising agent such as HNO_3 is added.

(c) F_2 is far too reactive — the reaction is violent and uncontrolled. Fluoroarenes are made another way (via diazonium salts).

Lesson 5

5

Friedel–Crafts: building C–C bonds

TEACHER COPY

Specification 6.1.1 (d)(iii) (g) — 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 (from the specification)

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

In plain English — by the end of this lesson I can…

- ☐ write equations for the alkylation and acylation of benzene
- ☐ identify the electrophile and draw the mechanism
- ☐ use the general pattern to predict products and mechanisms of unfamiliar reactions

Do now — retrieval (5 minutes)

Lesson 5

RETRIEVAL Lessons 2 and 4 — recall this first; today builds on it

1

What does a halogen carrier do?

Answer

Generates the electrophile (e.g. Br^+) by accepting a halide ion with its electron pair from Br_2.

2

Draw the intermediate in the bromination of benzene.

Answer

Ring with H and Br on the same carbon, horseshoe, + charge.

3

Name $C_6H_5COCH_3$.

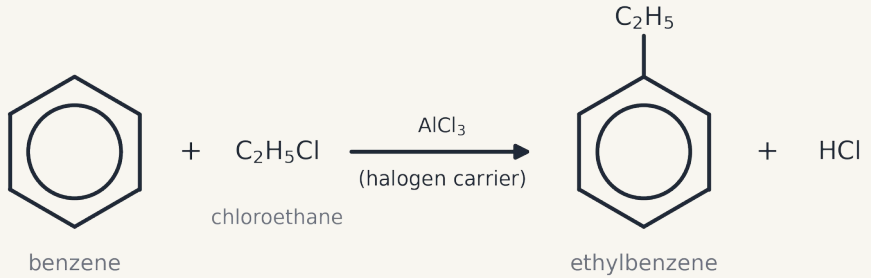
Answer

phenylethanone

Why make C–C bonds?

Lesson 5

SPEC (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



Synthesis often needs EXTRA carbon atoms added to a molecule.

Friedel–Crafts reactions (1877) make a new **C–C** bond to the ring.

Reagents: a **haloalkane** or an **acyl chloride** + an $AlCl_3$ halogen carrier.

alkylation: adding an alkyl group (e.g. $–C_2H_5$) to the ring

Question

In C_2H_5Cl, which end of the C–Cl bond is δ+? So which species could be the electrophile?

Answer

Carbon is δ+ (Cl is more electronegative). $AlCl_3$ removes Cl^- completely, leaving the carbocation $C_2H_5^+$ — the electrophile.

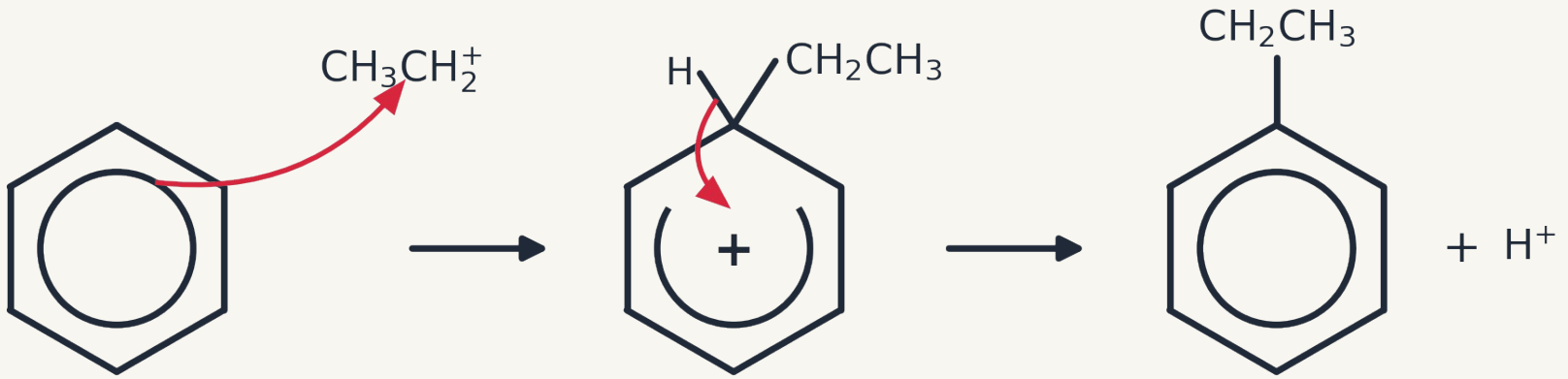
$C_2H_5Cl + AlCl_3 \rightarrow C_2H_5^+ + AlCl_4^-$

Alkylation: the mechanism

Lesson 5

SPEC (d(iii))(e)

(d(iii)) Friedel–Crafts: haloalkane or acyl chloride + halogen carrier; C–C bond formation for synthesis · (e) the mechanism of electrophilic substitution for nitration and halogenation



benzene intermediate

Question

Write the three steps (make the electrophile; substitution; regenerate the catalyst) for the alkylation of benzene with chloroethane.

Answer

Step 1: $C_2H_5Cl + AlCl_3 \rightarrow C_2H_5^+ + AlCl_4^-$

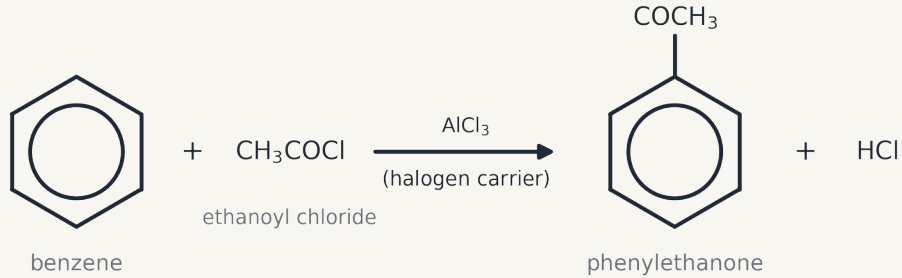
Step 2: the mechanism shown — same pattern as nitration and bromination.

Step 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Acylation

Lesson 5

SPEC (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



An acyl chloride, RCOCl, adds an acyl group and makes an aromatic **ketone**.

Benzene + ethanoyl chloride → **phenylethanone** + HCl ($AlCl_3$ catalyst).

The electrophile is the acylium ion, CH_3CO^+.

acylation: adding an acyl group, RCO–, to the ring

Question

Write the equation for the formation of the electrophile from CH_3COCl and $AlCl_3$.

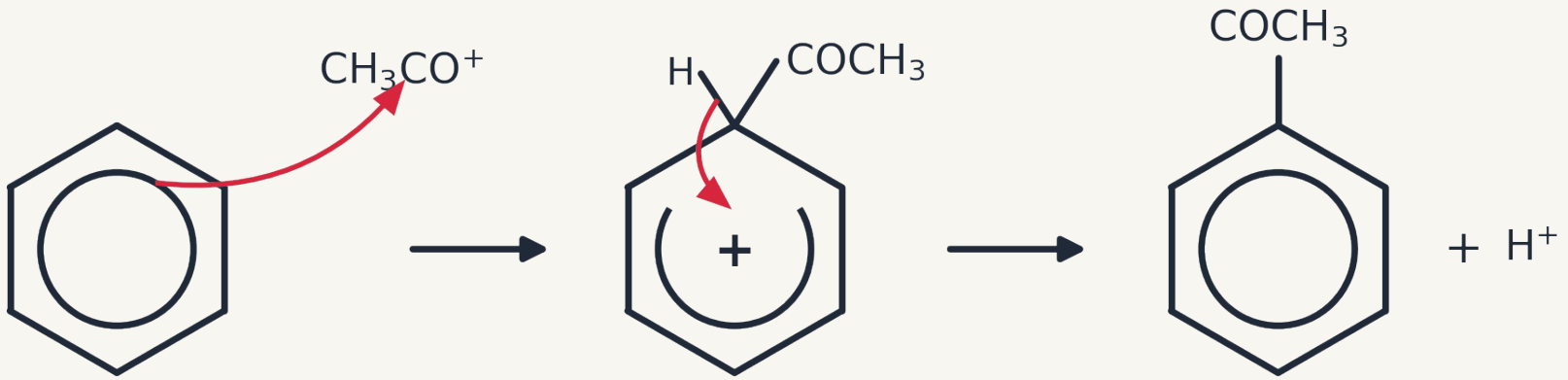
Answer

$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$

Acylation: the mechanism

Lesson 5

SPEC (e)(g) (e) the mechanism of electrophilic substitution for nitration and halogenation · (g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms



benzene intermediate

Question

Draw the mechanism for the acylation of benzene with CH_3CO^+ — same pattern!

Answer

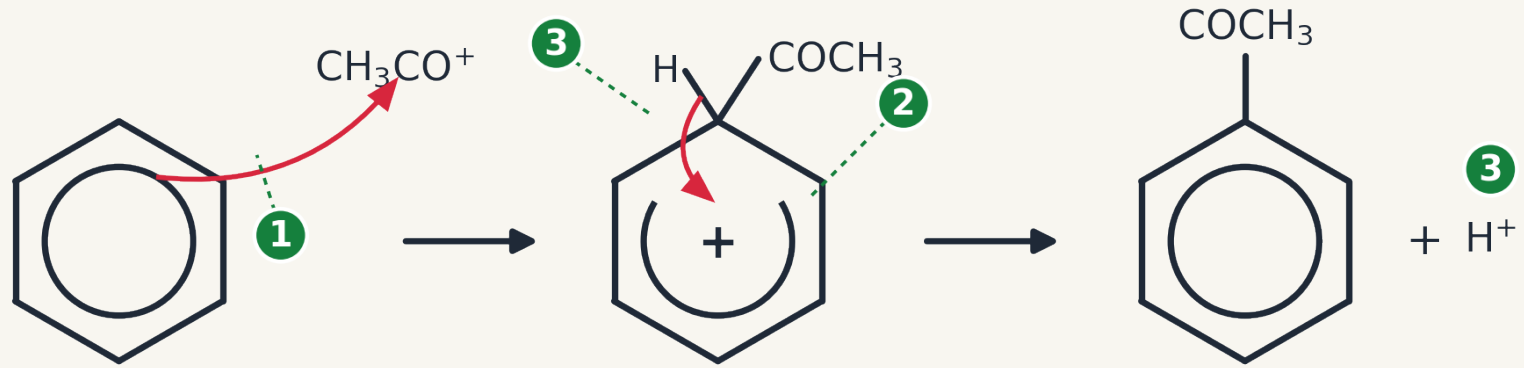
Arrow from ring to the C of CH_3CO^+ → intermediate (+, horseshoe, H and $COCH_3$ on the same carbon) → arrow from C–H bond into the ring → phenylethanone + H^+.

Then $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$.

The 3 marks — acylation

Lesson 5

SPEC (e)(g) (e) the mechanism of electrophilic substitution for nitration and halogenation · (g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms



benzene intermediate

① Arrow 1: tail **on the circle** (the electron pair), head **touching** the C=O carbon of CH_3CO^+ — the one with the +.

② Intermediate: **horseshoe** stopping either side of the carbon that holds the H and $COCH_3$; + **inside** it; H and $COCH_3$ on the **same carbon**.

③ Arrow 2: tail on the **middle of the C–H bond** (never the H), head **into the ring** towards the +. Products: phenylethanone + H^+.

Question

Which atom of CH_3CO^+ must arrow 1 touch, and why?

Answer

The carbonyl carbon: $CH_3–C^+=O$ — it is the atom carrying the positive charge.

Not the O and not the CH_3 carbon. Then: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$.

Now: your turn — Worksheet 5

Lesson 5

YOUR TURN Practise it now — (d(iii)) Friedel–Crafts: haloalkane or acyl chloride + halogen carrier; C–C bond formation for synthesis

N O W

Worksheet 5

Core questions 1–6

15 minutes

1 **Core** questions 1–6

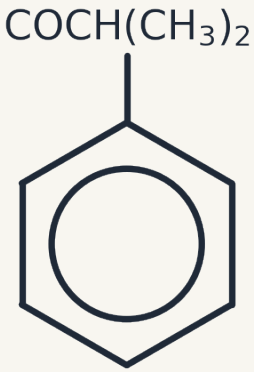
Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Predict the product

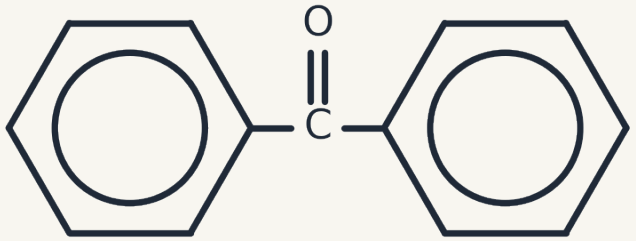
Lesson 5

SPEC (d(iii))(g)

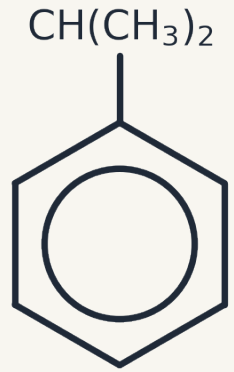
(d(iii)) Friedel–Crafts: haloalkane or acyl chloride + halogen carrier; C–C bond formation for synthesis · (g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms



A: from (CH3)2CHCOCl



B : from C_6H_5COCl



C: from 2-chloropropane

Question

Predict the organic product when benzene reacts, with $AlCl_3$, with: A $(CH_3)_2CHCOCl$ B C_6H_5COCl C 2-chloropropane, $CH_3CHClCH_3$

Answer

A: $C_6H_5COCH(CH_3)_2$ (a ketone, 2-methyl-1-phenylpropan-1-one).

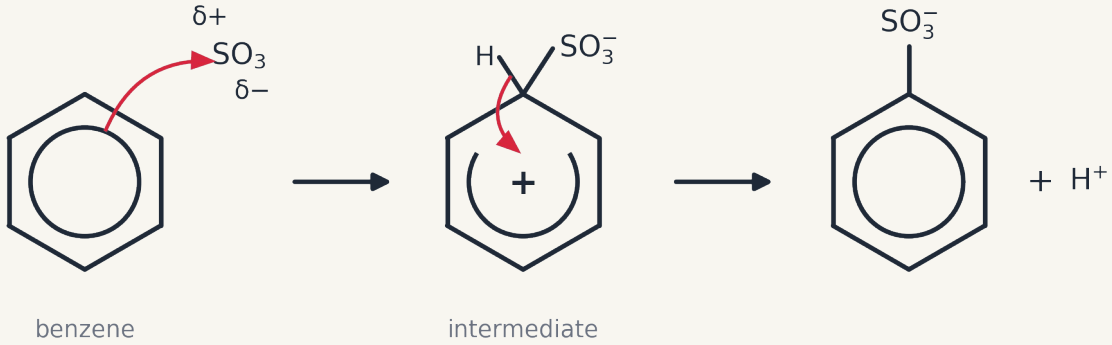
B: $(C_6H_5)_2CO$ — diphenylmethanone (two rings joined by C=O).

C: $C_6H_5CH(CH_3)_2$ — (1-methylethyl)benzene.

Unfamiliar reaction 1: sulfonation (spec g)

Lesson 5

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



Benzene + SO_3 (in fuming sulfuric acid) → benzenesulfonic acid, $C_6H_5SO_3H$ — used to make detergents.

The electrophile is SO_3: the S atom is δ+ because three oxygens pull electrons away.

Question

Complete the mechanism. Which atom does the ring attack? Where does the + charge go? What happens to the product ion?

Answer

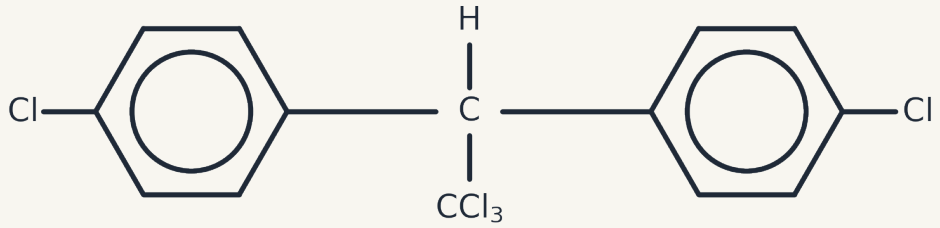
The ring attacks the δ+ sulfur; the intermediate carries the + charge in the ring and a $–SO_3^-$ group.

Loss of H^+ gives $C_6H_5SO_3^-$, which picks up H^+ to form benzenesulfonic acid, $C_6H_5SO_3H$.

Unfamiliar reaction 2: making DDT

Lesson 5

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



DDT

Chlorobenzene reacts with trichloroethanal, Cl_3CCHO, (H_2SO_4 catalyst) to make the insecticide DDT.

Two rings join to the same carbon; water is lost.

Question

Construct a balanced equation for the formation of DDT from chlorobenzene and Cl_3CCHO.

Answer

$2C_6H_5Cl + Cl_3CCHO \rightarrow (ClC_6H_4)_2CHCCl_3 + H_2O$

Each ring is substituted at position 4 (opposite the Cl).

Now: your turn — Worksheet 5

Lesson 5

YOUR TURN Practise it now — (g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms

NOW

Worksheet 5

Harder H1–H4 (core done)

10 minutes

1 **Core** Harder H1–H4 (core done)

2 **Then** Exam-style E1 — in class, in silence, in one go

3 **Finished those?** Uni worksheet U5 Friedel–Crafts: the fine print (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Exit ticket

Lesson 5

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

1 [2 marks]

Write an equation for the reaction of benzene with 2-chloropropane in the presence of $AlCl_3$.

Answer

$C_6H_6 + CH_3CHClCH_3 \rightarrow C_6H_5CH(CH_3)_2 + HCl$

2 [2 marks]

Identify the electrophile in the acylation of benzene with ethanoyl chloride and write an equation for its formation.

Answer

CH_3CO^+; $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$

3 [1 mark]

Why are Friedel–Crafts reactions important in organic synthesis?

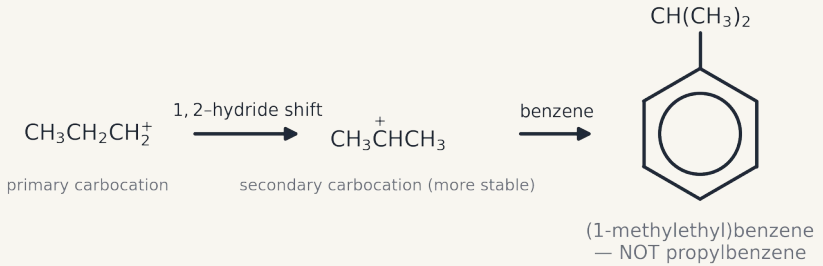
Answer

They form a C–C bond to the ring, so carbon atoms can be added / the carbon skeleton extended.

STRETCH: Friedel–Crafts — the fine print

Lesson 5

BEYOND THE SPEC Extension — not examined. Stretch Pack §5



Four things the A-level story leaves out:

1. Rearrangement — 1-chloropropane gives mostly (1-methylethyl)benzene (primary carbocation → more stable secondary).
2. Polyalkylation — alkyl groups activate the ring, so the product reacts faster than benzene.
3. Deactivated rings (nitrobenzene) do not react. 4. –NH_2 groups poison the catalyst (lone pair binds $AlCl_3$).

Stretch

How would you make propylbenzene (a straight three-carbon chain) from benzene in TWO steps?

Answer

Acylate with $CH_3CH_2COCl/AlCl_3$ — acylium ions do not rearrange, and the ketone product is deactivated (no over-reaction).

Then reduce C=O to CH_2: Clemmensen (Zn/Hg, HCl) or Wolff–Kishner (N_2H_4, KOH).

Lesson 6

6 Phenol

TEACHER COPY

Specification 6.1.1 (h) (i) (j) — 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 (from the specification)

- 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.

In plain English — by the end of this lesson I can…

- ☐ describe phenol as a weak acid: reacts with NaOH but NOT with carbonates
- ☐ write equations for phenol with bromine and with dilute nitric acid
- ☐ explain why phenol is more reactive than benzene

Do now — retrieval (5 minutes)

Lesson 6

RETRIEVAL 5.1.3 acids — recall this first; today builds on it

1

What is a weak acid?

Answer

An acid that only PARTIALLY dissociates in water.

2

What do you observe when a carboxylic acid is added to sodium carbonate solution?

Answer

Fizzing / effervescence — CO_2 gas is given off.

3

Name C_6H_5OH.

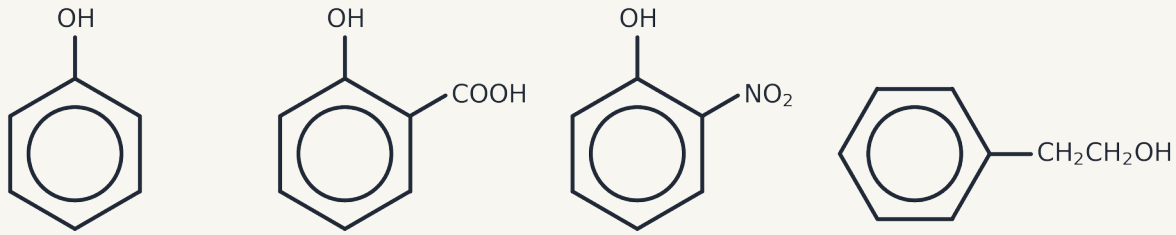
Answer

phenol

What is a phenol?

Lesson 6

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



phenol | 2-hydroxybenzoic acid | 2-nitrophenol | 2-phenylethanol

A phenol has an –OH group bonded **directly** to the benzene ring.

If the –OH is on a side chain it is an **alcohol** and reacts like one.

Uses: antiseptics (TCP), disinfectants, plastics and aspirin.

phenol: an –OH group attached directly to a benzene ring

Question

Which of A–D is NOT a phenol? How can you tell?

Answer

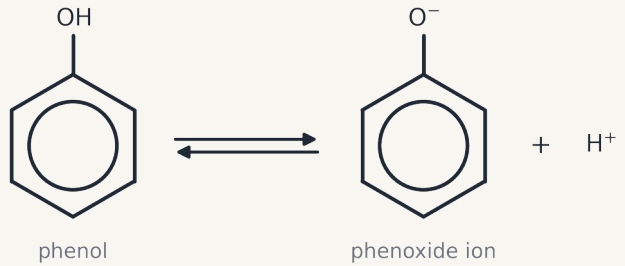
D (2-phenylethanol) — its –OH is on the CH_2CH_2 chain, not on the ring. It is an aromatic alcohol.

A phenol; B 2-hydroxybenzoic acid; C 2-nitrophenol.

Phenol is a weak acid

Lesson 6

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



Question

Phenol PARTIALLY dissociates in water. Use K_a to put ethanol, phenol and ethanoic acid in order of acid strength (strongest first).

Compound	K_a at 298 K / mol dm^{-3}	Order
ethanol	1.0×10^{-16}	**3 (weakest)**
phenol	1.3×10^{-10}	**2**
ethanoic acid	1.7×10^{-5}	**1 (strongest)**

Answer

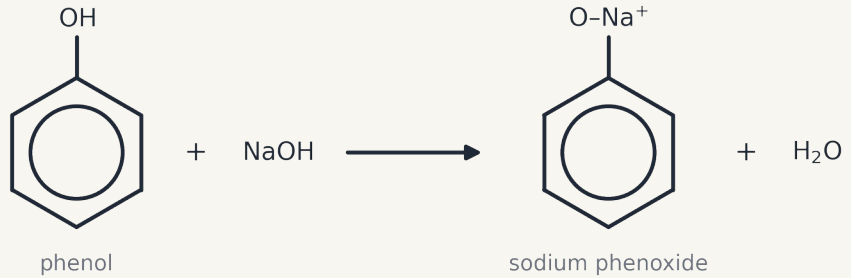
ethanoic acid > phenol > ethanol.

Larger K_a = more dissociation = stronger acid.

Reactions with bases — a test for phenols

Lesson 6

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



Phenol + NaOH → sodium phenoxide + water (neutralisation).

Phenol + Na_2CO_3 → **no reaction**: phenol is too weak an acid to release CO_2 from a carbonate.

Carboxylic acids DO react with carbonates.

Question

You have two unlabelled bottles of white solid: phenol and benzoic acid. Describe a simple test to tell them apart.

Answer

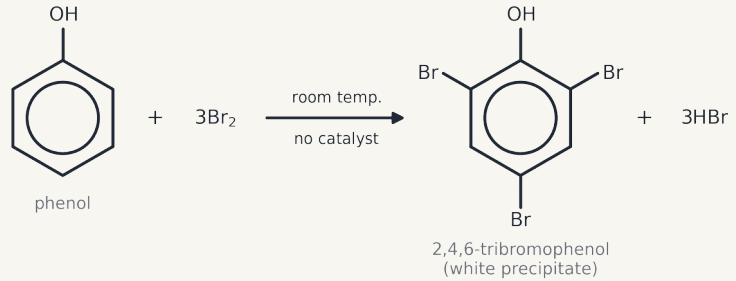
Add Na_2CO_3(aq) (or $NaHCO_3$): benzoic acid fizzes (CO_2 — turns limewater milky); phenol does not.

(Both dissolve in NaOH(aq), so NaOH would not tell them apart.)

Phenol + bromine

Lesson 6

SPEC (i(i)) the electrophilic substitution reaction of phenol with bromine to form 2,4,6-tribromophenol



Phenol reacts with bromine water at room temperature with NO catalyst.

Observations: bromine is **decolourised** and a **white precipitate** of 2,4,6-tribromophenol forms.

Question

List THREE differences between the bromination of phenol and the bromination of benzene.

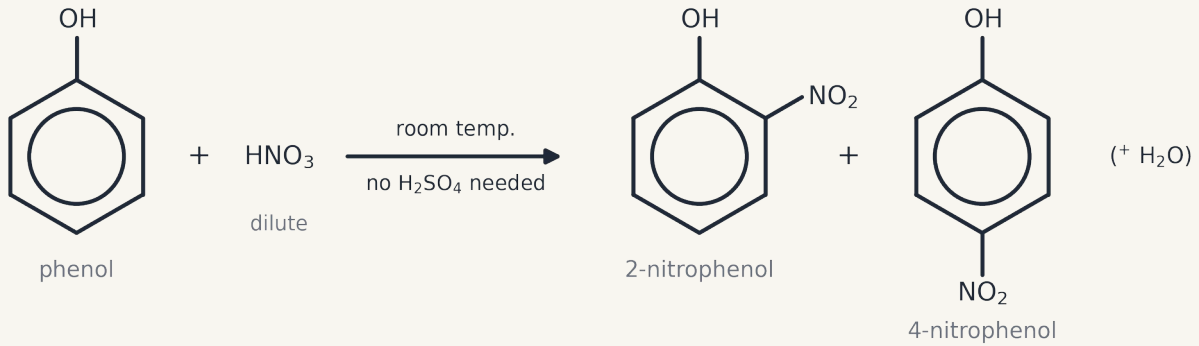
Answer

1. No halogen carrier needed (benzene needs $FeBr_3$).
2. Room temperature, with aqueous bromine; visible change (decolourised + white ppt).
3. THREE Br atoms substitute (2, 4, 6) — benzene gives just one bromobenzene.

Phenol + nitric acid

Lesson 6

SPEC (i(ii)) the electrophilic substitution reaction of phenol with dilute nitric acid to form a mixture of 2-nitrophenol and 4-nitrophenol



Phenol reacts with **dilute** HNO_3 at room temperature — no concentrated H_2SO_4 needed.

Products: a mixture of **2-nitrophenol** and **4-nitrophenol**.

Question

Benzene needs concentrated HNO_3 AND concentrated H_2SO_4 at 50 °C. What does this tell you about phenol's ring?

Answer

Phenol's ring is much more susceptible to attack by electrophiles (it is activated).

Even the weaker electrophile present in dilute acid can attack it.

Now: your turn — Worksheet 6

Lesson 6

YOUR TURN

Practise it now — (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

N O W

Worksheet 6

Core questions 1–3 and 6–7

12 minutes

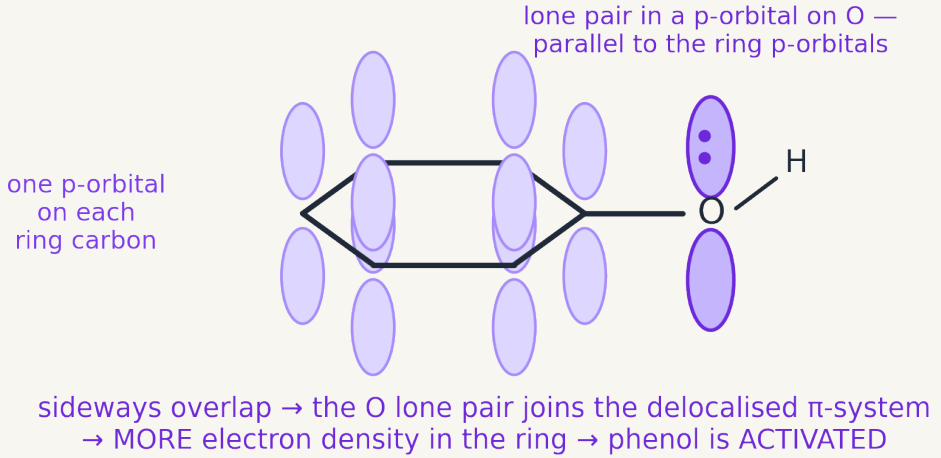
1 **Core** questions 1–3 and 6–7

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Why is phenol more reactive? (spec j)

Lesson 6

SPEC (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



sideways overlap → the O lone pair joins the delocalised π-system → MORE electron density in the ring → phenol is ACTIVATED

activated ring: a ring with higher electron density, so it is more susceptible to electrophiles

One **lone pair** on the oxygen is in a **p-orbital** that overlaps with the ring's π-system.

Electron density is DONATED into the ring.

Question

Explain in THREE steps why phenol reacts with bromine but benzene does not.

Answer

1. An oxygen lone pair (in a p-orbital) is partially delocalised into the ring.
2. The electron density of the ring INCREASES — the ring is activated.
3. The ring can now POLARISE Br_2 (induce a dipole) → attack by the electrophile — no catalyst needed.

Summary: benzene vs phenol with bromine

Lesson 6

SPEC (f)(i)(j)

(f) why benzene resists bromination compared with alkenes: delocalised vs localised π electron density · (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

Question

Complete the table from memory.

	Benzene	Phenol
Conditions	**room temp., Br_2 (liquid)**	**room temp., Br_2(aq)**
Catalyst	**halogen carrier, e.g. $FeBr_3$**	**none**
Observation	**none visible (HBr fumes)**	**Br_2 decolourised; white precipitate**
Product	**bromobenzene (one Br)**	**2,4,6-tribromophenol (three Br)**
Why?	**delocalised π electrons; low electron density**	**O lone pair donated into ring; higher electron density**

Now: your turn — Worksheet 6

Lesson 6

YOUR TURN Practise it now — (j) phenol is more easily substituted than benzene: electron pair donated from an oxygen p-orbital into the π-system

N O W

Worksheet 6

Core questions 4–5

10 minutes

1. **Core** questions 4–5
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U6 Phenol: acidity explained properly (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Exit ticket

Lesson 6

SPEC CHECK (h)(i)(j) (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

1 [1 mark]

Write an equation for the reaction of phenol with sodium hydroxide.

Answer

$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$

2 [3 marks]

State what you would SEE when bromine water is added to phenol, and write the equation.

Answer

Bromine decolourised (orange → colourless); white precipitate.
$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$ (2,4,6-tribromophenol).

3 [3 marks]

Explain why phenol reacts more readily than benzene with electrophiles.

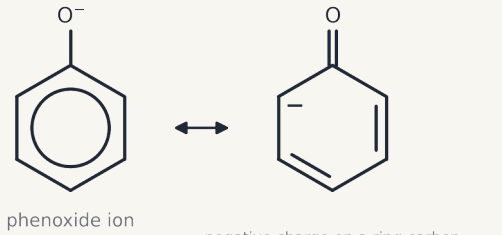
Answer

O lone pair in a p-orbital is delocalised into the ring → increases electron density → ring more susceptible to attack / can polarise Br_2.

STRETCH: why is phenol acidic at all?

Lesson 6

BEYOND THE SPEC Extension — not examined. Stretch Pack §6



pK_a: ethanol ≈ 16, phenol ≈ 10, ethanoic acid ≈ 4.8.

The phenoxide ion is stabilised because the negative charge on O is delocalised into the ring (resonance), so the equilibrium lies further right than for an alcohol.

Stretch

(a) 4-Nitrophenol has pK_a 7.2. Is it a stronger or weaker acid than phenol? Explain. (b) Phenol's –OH activates the ring — what would you predict about the phenoxide ion, $C_6H_5O^-$?

Answer

(a) Stronger (lower pK_a): $-NO_2$ withdraws electrons and delocalises the negative charge onto its oxygens → phenoxide more stable → more dissociation.

(b) O^- donates a full negative charge → far more electron density in the ring → even more reactive (phenol brominates faster in alkali).

7

Lesson 7

TEACHER COPY

Directing groups and synthesis

Specification 6.1.1 (k) (l) — 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 (from the specification)

- 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.

In plain English — by the end of this lesson I can…

- ☐ state which groups direct to positions 2,4 and which direct to position 3
- ☐ predict the products of substitution reactions
- ☐ plan a two-step synthesis in the RIGHT order

Do now — retrieval (5 minutes)

Lesson 7

RETRIEVAL Lessons 2 and 6 — recall this first; today builds on it

1

Which is more reactive with bromine: phenol or benzene? Why?

Answer

Phenol — O lone pair donated into the ring increases electron density.

2

Name the product of phenol + excess bromine water.

Answer

2,4,6-tribromophenol

3

Name $C_6H_5NH_2$.

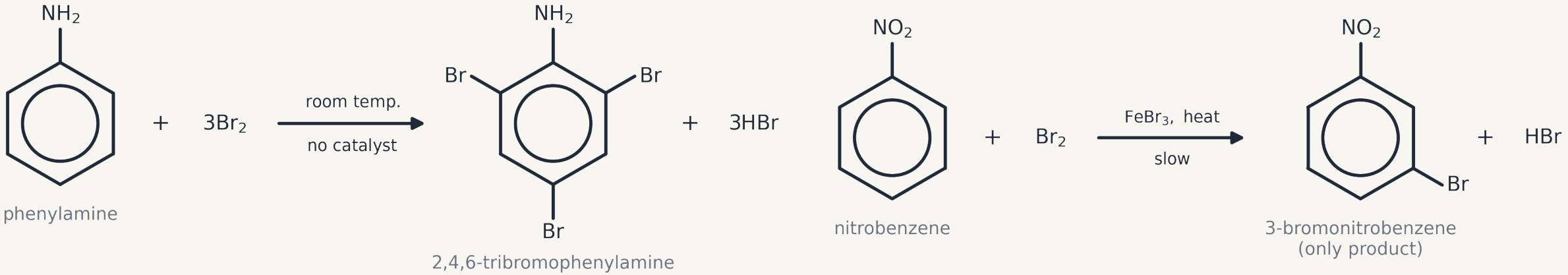
Answer

phenylamine

Activating and deactivating groups

Lesson 7

SPEC (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



phenylamine

2,4,6-tribromophenylamine

nitrobenzene

3-bromonitrobenzene (only product)

Question

Compare the two reactions: conditions, how many groups are added, and WHERE they go.

directing group: a group already on the ring that decides where the next group goes

Answer

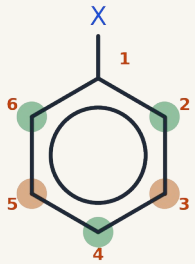
Phenylamine: no catalyst, room temp., THREE Br added at positions 2, 4, 6 → $–NH_2$ ACTIVATES the ring.

Nitrobenzene: catalyst + heat, slow, ONE Br at position 3 → $–NO_2$ DEACTIVATES the ring.

The directing rule (spec k)

Lesson 7

SPEC (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



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

Electron-**donating** groups (–OH, $–NH_2$): activate the ring → direct to positions **2 and 4**.

Electron-**withdrawing** groups ($–NO_2$): deactivate the ring → direct to position **3**.

Only KNOW these: OH, NH_2 → 2,4-directing; NO_2 → 3-directing. Others are given in the exam.

Question

Which positions are 'ortho' and 'para' to X? Which are 'meta'? Why do we only ever say '2 and 4', never '6'?

Answer

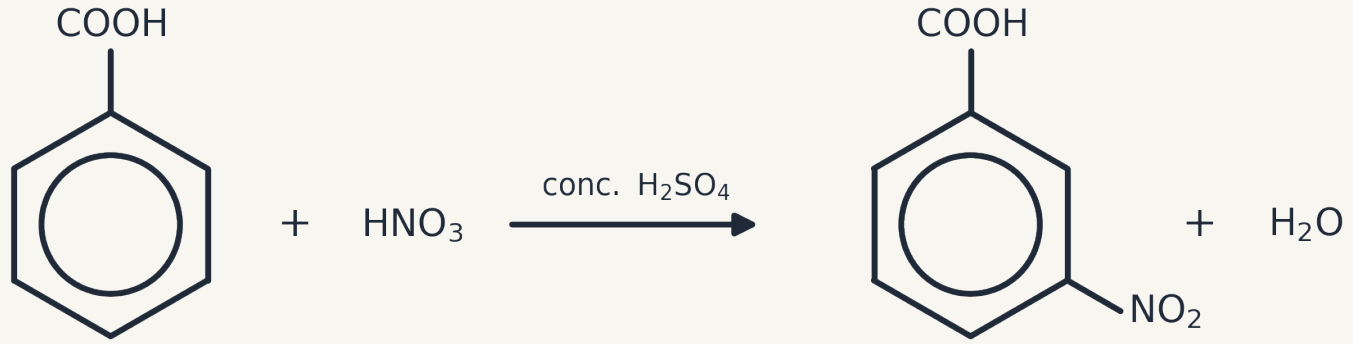
2 and 6 = ortho; 4 = para; 3 and 5 = meta.

2 and 6 are equivalent (mirror images), as are 3 and 5 — so we quote the lowest numbers: 2,4- and 3-.

Predicting products 1

Lesson 7

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



benzoic acid — 3-nitrobenzoic acid

Data given in the question: –COOH is 3-directing.

Question

Benzoic acid is nitrated with HNO_3/H_2SO_4. Draw the mono-substituted organic product and write the equation.

Answer

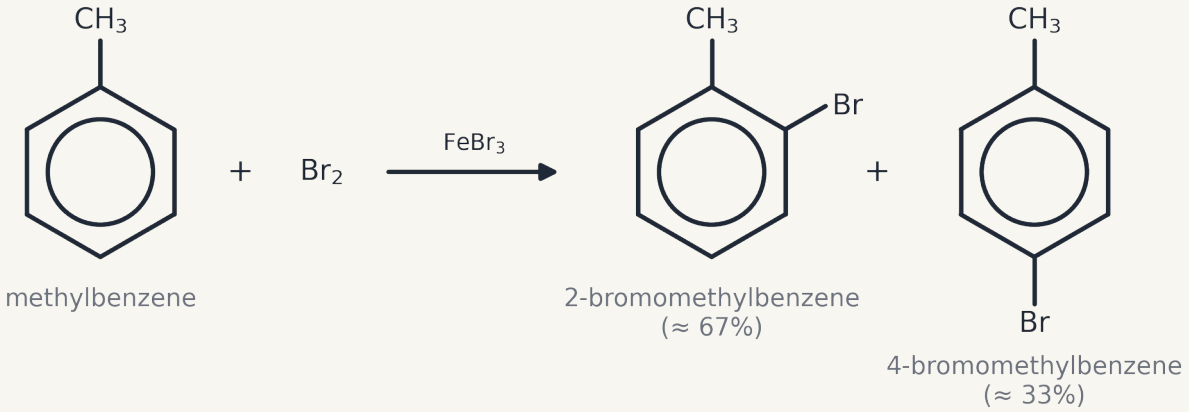
3-nitrobenzoic acid (NO_2 on carbon 3).

$C_6H_5COOH + HNO_3 \rightarrow C_6H_4(NO_2)COOH + H_2O$

Predicting products 2: why TWO products?

Lesson 7

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



Data: –CH_3 is 2,4-directing. Methylbenzene + Br_2/$FeBr_3$ gives about 67% of one product and 33% of another.

? Question

Draw both products. Why is roughly TWICE as much of one formed?

Answer

2-bromomethylbenzene (≈67%) and 4-bromomethylbenzene (≈33%).

Positions 2 and 6 are equivalent — two ways to make the '2' product — but there is only ONE position 4 → about 2 : 1.

Now: your turn — Worksheet 7

Lesson 7

YOUR TURN Practise it now — (k) OH and NH_2 (electron-donating) direct to 2- and 4-; NO_2 (electron-withdrawing) directs to 3-

N O W

Worksheet 7

Core questions 1–2 and 4–5

12 minutes

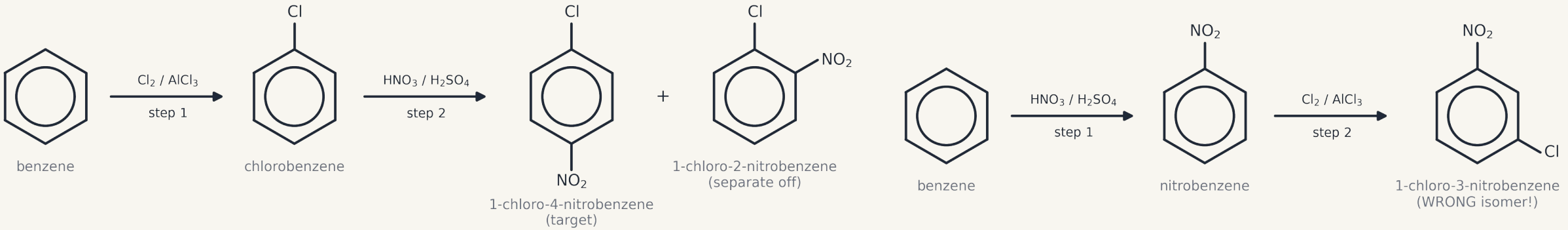
1 **Core** questions 1–2 and 4–5

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Planning a synthesis: order matters! (spec l)

Lesson 7

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



Question

Target: 1-chloro-4-nitrobenzene from benzene. Which group must go on FIRST, and why?

Answer

Chlorinate FIRST (Cl_2/$AlCl_3$): Cl is 2,4-directing, so nitration then puts NO_2 at position 4 (plus some 2-).

If you nitrate first, NO_2 is 3-directing → Cl goes to position 3 → the WRONG isomer.

Separate the 2-/4- mixture by distillation or recrystallisation.

Your turn: two-step syntheses

Lesson 7

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

Question

Starting from benzene, suggest reagents, conditions and the ORDER of steps to make:
(a) 3-nitromethylbenzene (b) 2-nitromethylbenzene

Stretch: In real labs, Friedel–Crafts fails on nitrobenzene (the ring is too deactivated) — route (a) is an A-level answer, not an industrial one. Ask the G&T student how a chemist might really make it.

Answer

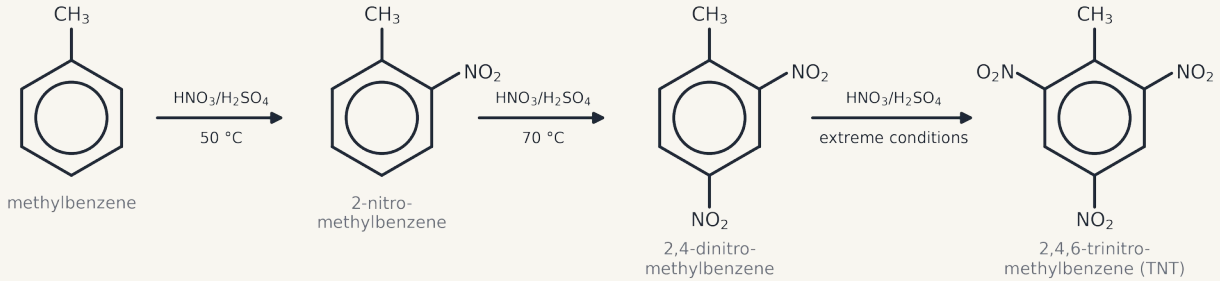
(a) NO_2 must direct the CH_3 to position 3 → nitrate first (conc. HNO_3/H_2SO_4, 50 °C), then $CH_3Cl/AlCl_3$.

(b) CH_3 must direct the NO_2 to position 2 → alkylate first ($CH_3Cl/AlCl_3$), then nitrate (conc. HNO_3/H_2SO_4, 50 °C); separate the 2- from the 4- isomer.

The TNT story

Lesson 7

SPEC (k)(l) (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



Methylbenzene is nitrated three times to make 2,4,6-trinitromethylbenzene (TNT).

Each step needs **harsher** conditions: 50 °C, then 70 °C, then extreme conditions.

Question

Explain why each successive nitration is harder, and why the temperature must be controlled so carefully.

Answer

Each –NO_2 group withdraws electron density → the ring is less susceptible to attack → higher temperature / more concentrated acid needed.

Over-heating risks a runaway reaction (explosion) and gives mixtures of products.

Now: your turn — Worksheet 7

Lesson 7

YOUR TURN Practise it now — (I) predicting substitution products from directing effects; importance to organic synthesis

N O W

Worksheet 7

Core question 3 (two-step syntheses)

8 minutes

1. **Core** question 3 (two-step syntheses)
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U7 Directing effects: the real reason (purple, not examined)

Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Exit ticket

Lesson 7

SPEC CHECK (k)(l) (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

1 [1 mark]

Classify –OH, $–NO_2$ and $–NH_2$ as 2,4-directing or 3-directing.

Answer

–OH and $–NH_2$: 2,4-directing. $–NO_2$: 3-directing.

2 [2 marks]

Draw the organic product(s) of: (a) phenol + dilute HNO_3 (b) nitrobenzene + $Br_2/FeBr_3$.

Answer

(a) 2-nitrophenol and 4-nitrophenol. (b) 3-bromonitrobenzene.

3 [2 marks]

Suggest a two-step synthesis of 1-bromo-4-nitrobenzene from benzene.

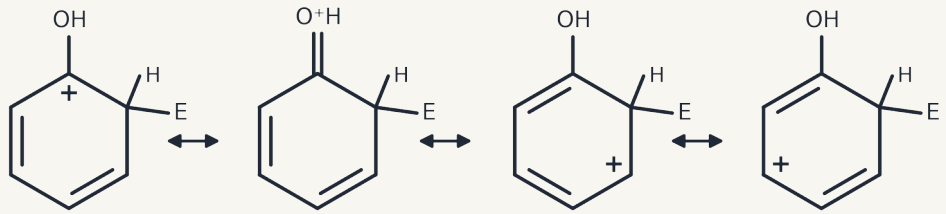
Answer

Step 1: $Br_2/FeBr_3$ → bromobenzene. Step 2: conc. HNO_3/H_2SO_4, 50 °C → 1-bromo-4-nitrobenzene (+ 2-isomer). Br is 2,4-directing (data would be given).

STRETCH: the real reason for directing effects

Lesson 7

BEYOND THE SPEC Extension — not examined. Stretch Pack §4



attack at position 2 (ortho): the oxygen lone pair gives a FOURTH resonance form — every atom has a full octet

Draw the intermediate for attack at each position. For –OH or –NH_2, attack at 2 or 4 gives an EXTRA resonance form in which the lone pair on O/N stabilises the positive charge. Attack at 3 does not.

Stretch

(a) Halogens DEACTIVATE the ring yet direct 2,4-. Explain. (b) Predict where –SO_3H directs, and why.

Answer

(a) Inductive effect: halogens are electronegative → withdraw electron density → deactivate. But their lone pairs still donate by resonance into the 2,4-intermediates → 2,4-directing.

(b) 3-directing: S is δ+ and withdraws electrons; the 2- and 4-intermediates would put the + charge next to δ+ S — destabilised.

Final section

TEACHER COPY

Summary and exam clinic

Specification 6.1.1 (a)–(l) — 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

Examiner guidance (from the specification)

- The guidance for each statement is on that lesson's section slide.
- The exam clinic questions are adapted from OCR F324 past papers — the same examiners, the same mark points.

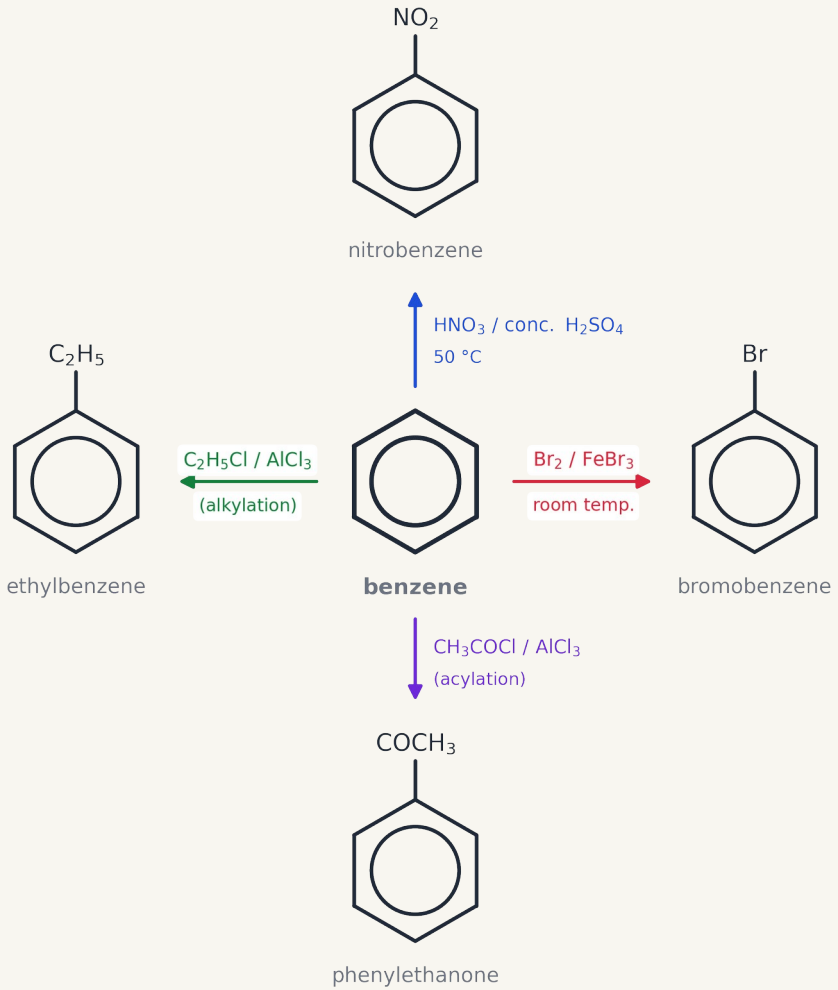
In plain English — by the end of this lesson I can…

- ☐ draw the reaction map for benzene and for phenol
- ☐ tackle exam questions that combine several ideas
- ☐ self-assess against every spec statement

The big picture: benzene

Summary

SPEC (d) the electrophilic substitution of aromatic compounds with (i) concentrated nitric acid in the presence of concentrated sulfuric acid, (ii) a halogen in the presence of a halogen carrier, (iii) a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel–Crafts reaction)



Question

Student copy: write the reagents and conditions on each arrow. Then: which of these four reactions need a halogen carrier? Which one adds a C=O group?

Answer

Bromination, alkylation and acylation all need a halogen carrier ($FeBr_3$ / $AlCl_3$). Nitration uses conc. H_2SO_4 instead.

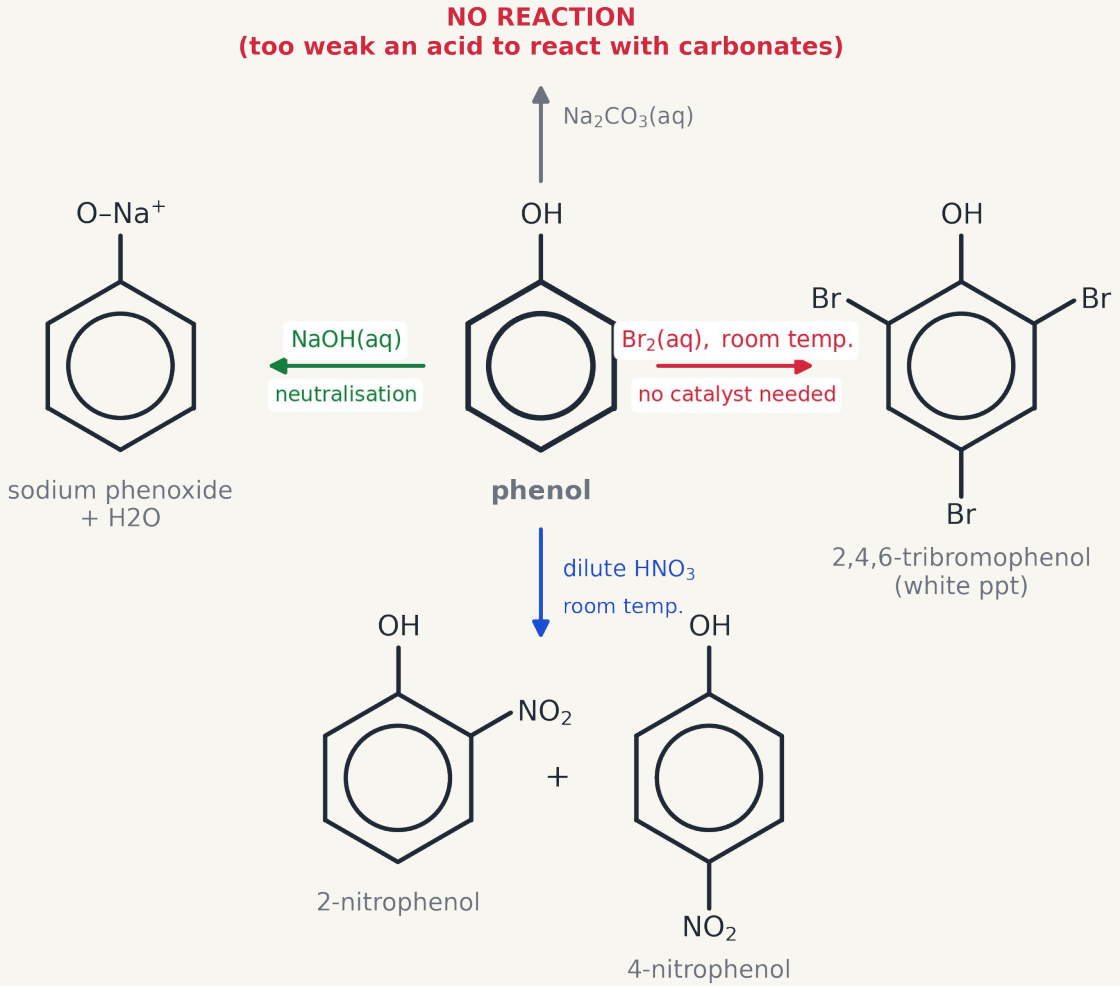
Acylation ($CH_3COCl/AlCl_3$) adds C=O (a ketone: phenylethanone).

The big picture: phenol

Summary

SPEC (h)(i)(j)

(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



Question

Student copy: fill in the reagents on each arrow. Which reaction tells you phenol is a WEAK acid? Which reactions show the ring is ACTIVATED?

Answer

Weak acid: reacts with NaOH (neutralisation) but NOT with Na_2CO_3.

Activated ring: bromination with no catalyst (three Br) and nitration with DILUTE nitric acid.

Mechanism marks: the checklist

Summary

SPEC (e)(g) (e) the mechanism of electrophilic substitution for nitration and halogenation · (g) interpreting unfamiliar electrophilic substitution reactions, including predicting mechanisms

Question

Cover the table. Say all six lines from memory.

Mark	The examiner must see
1	Equation making the electrophile (e.g. $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$)
2	Arrow 1: tail ON the circle, head TOUCHING the atom with the +
3	Horseshoe stops either side of the carbon holding H and the new group; + INSIDE it
4	H AND the new group on the SAME carbon
5	Arrow 2: tail on the MIDDLE of the C–H bond, head INTO the ring
6	Product + H^+ ; catalyst regenerated ($H^+ + HSO_4^- \rightarrow H_2SO_4$)

Answer

Most common losses: head not on the atom with the +; + written outside the horseshoe; arrow 2 from the H instead of the C–H bond; no H^+ in the products.

Now: your turn — Worksheet 8

Summary

YOUR TURN Practise it now — (a) Kekulé model vs delocalised model: p-orbital overlap → delocalised π-system · (l) predicting substitution products from directing effects; importance to organic synthesis

N O W

Worksheet 8

Chapter practice questions 1–9 (textbook pp. 451–453), 72 marks

80 minutes, in one sitting

1 **Core** Chapter practice questions 1–9 (textbook pp. 451–453), 72 marks

2 **Finished those?** Uni worksheet the whole Uni worksheet, then the Stretch Pack (purple, not examined)

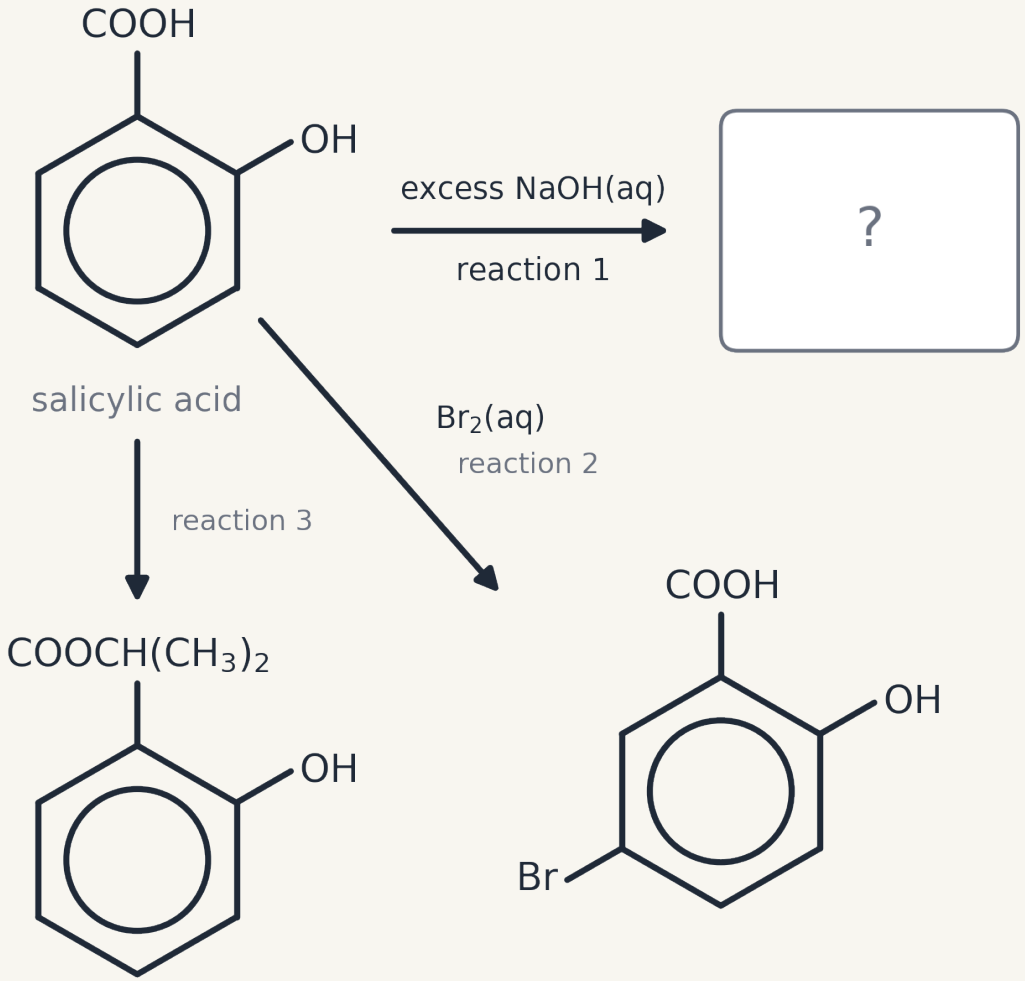
Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

Exam clinic 1: salicylic acid (OCR F324 style)

Summary

SPEC (h)(i)(j)

(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



Question

(i) Draw the product of reaction 1 (excess NaOH). (ii) Write an equation for reaction 2. (iii) Give reagents/conditions for reaction 3. (iv) Why does bromine react more readily with salicylic acid than with benzene?

Answer

(i) Both acidic H's removed: $–COO^-Na^+$ and $–O^-Na^+$ (the phenol –OH is acidic enough for NaOH).

(ii) $HOC_6H_4COOH + Br_2 \rightarrow HOC_6H_3(Br)COOH + HBr$ (no catalyst; Br at position 5, i.e. para to OH).

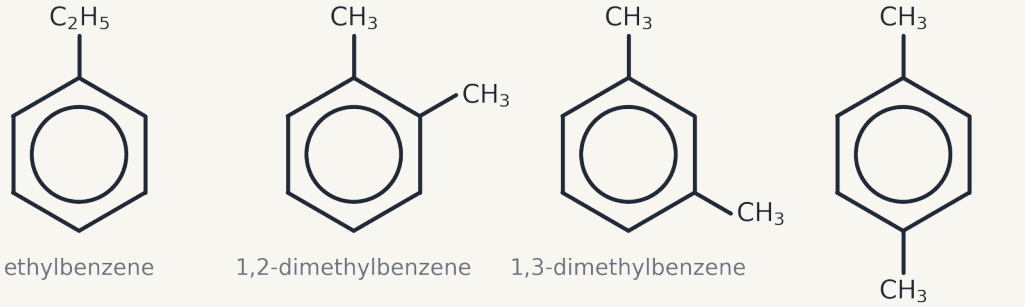
(iii) Propan-2-ol with conc. H_2SO_4 catalyst, heat under reflux (esterification).

(iv) O lone pair delocalised into the ring → higher electron density → polarises Br_2 → attack without a catalyst.

Exam clinic 2: the C_8H_{10} puzzle

Summary

SPEC (c)(l) (c) IUPAC rules for naming substituted aromatic compounds · (l) predicting substitution products from directing effects; importance to organic synthesis



An aromatic hydrocarbon has M = 106 (mass spectrum) and is 90.56% C, 9.44% H by mass.

Question

(a) Find the molecular formula. (b) Draw ALL the structural isomers that contain a benzene ring. (c) Isomer A gives only ONE mono-nitro product with HNO_3/H_2SO_4. Identify A and the product B.

Answer

(a) C: 90.56/12 = 7.55; H: 9.44/1 = 9.44 → ratio 1 : 1.25 = 4 : 5 → C_4H_5 (Mr 53) → ×2 = C_8H_{10}.

(b) ethylbenzene; 1,2-, 1,3- and 1,4-dimethylbenzene (four isomers).

(c) A = 1,4-dimethylbenzene (every ring H is equivalent → one product). B = 1,4-dimethyl-2-nitrobenzene.

Self-assessment: I can…

Summary

SPEC 6.1.1 (a)–(l) Every learning outcome in 6.1.1 Aromatic compounds — rate yourself against each one

(a)	describe the Kekulé and delocalised models of benzene (p-orbital overlap → π-system)	☐ ☐ ☐
(b)	explain the evidence: bond lengths, enthalpy of hydrogenation, resistance to reaction	☐ ☐ ☐
(c)	name substituted aromatic compounds using IUPAC rules and locants	☐ ☐ ☐
(d)	give reagents/conditions for nitration, halogenation, alkylation and acylation	☐ ☐ ☐
(e)	draw the mechanism for nitration and halogenation, including forming the electrophile	☐ ☐ ☐
(f)	explain why benzene resists bromination compared with alkenes	☐ ☐ ☐
(g)	predict the products and mechanism of an unfamiliar electrophilic substitution	☐ ☐ ☐
(h)	describe phenol as a weak acid (NaOH: yes; carbonates: no)	☐ ☐ ☐
(i)	write equations for phenol + Br_2 (2,4,6-tribromophenol) and phenol + dilute HNO_3 (2- and 4-nitrophenol)	☐ ☐ ☐
(j)	explain why phenol is more reactive than benzene (O lone pair → π-system)	☐ ☐ ☐
(k)	state that OH/NH_2 are 2,4-directing and NO_2 is 3-directing	☐ ☐ ☐
(l)	predict substitution products and plan the ORDER of a two-step synthesis	☐ ☐ ☐

Tick RED (not yet) / AMBER (nearly) / GREEN (confident) for each spec statement — then choose one red or amber to revise first.