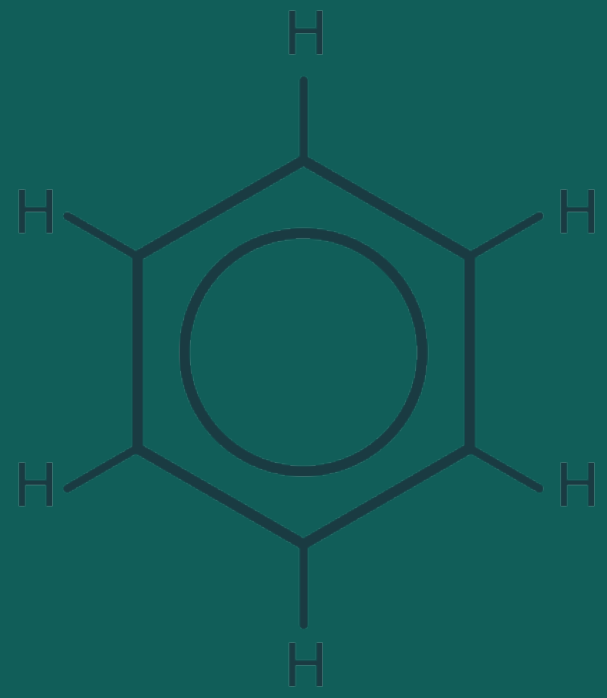
Aromatic Chemistry

Benzene, electrophilic substitution, phenol and directing groups

OCR A Level Chemistry A (H432) — Module 6.1.1



STUDENT COPY — fill in the gaps

Name: _____ Class: _____

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

STUDENT 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?

Your answer

2

What is an electrophile?

Your answer

3

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

Your answer

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 _____.

A colourless, sweet-smelling, _____ liquid.

Found in crude oil, petrol and cigarette smoke.

It is a _____ — 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?

Your answer

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 _____ ring of six carbon atoms.

The ring has _____ single and double bonds.

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

Question

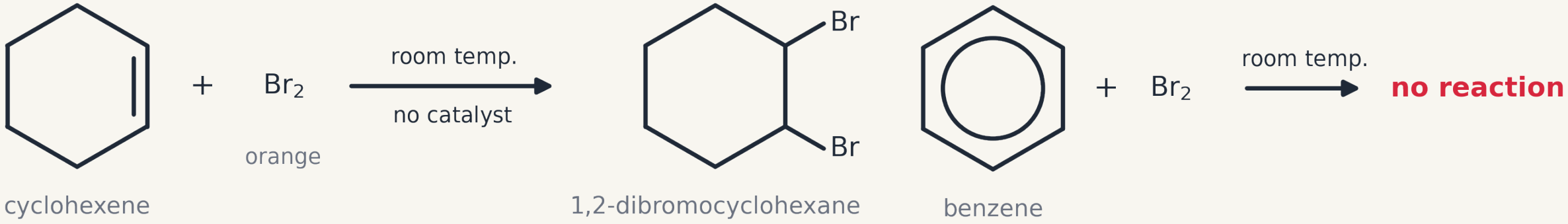
If Kekulé were right, benzene would have THREE C=C bonds.
Predict what should happen when bromine water is added.

Your answer

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



cyclohexene

1,2-dibromocyclohexane

benzene

Question

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

Your answer

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 _____ measured the bonds in benzene using _____.

Question

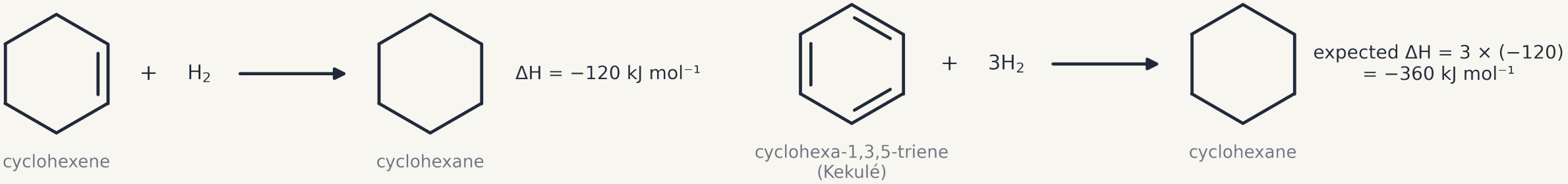
A C–C single bond is 0.153 nm and a C=C double bond is 0.134 nm. What did Lonsdale find, and what does it mean?

Your answer

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 = _____ kJ mol^{-1}.

hydrogenation: adding hydrogen to an unsaturated compound

Question

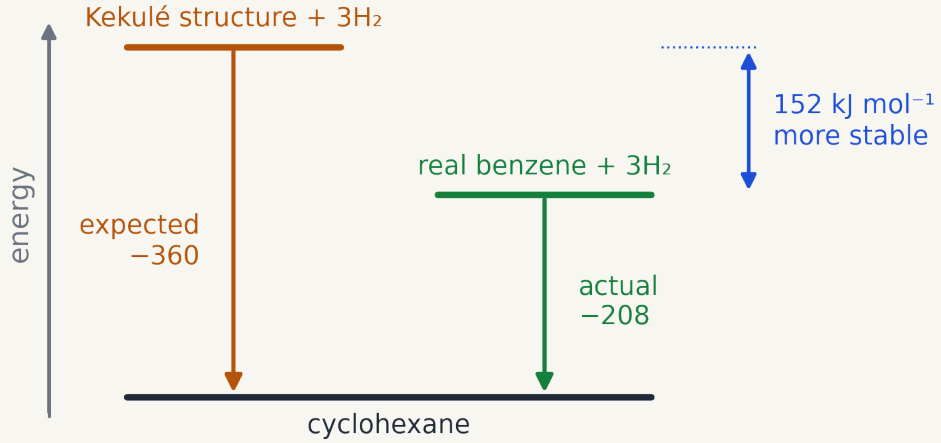
Kekulé's benzene (cyclohexa-1,3,5-triene) has THREE C=C bonds. Predict its enthalpy change of hydrogenation.

Your answer

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 = _____ 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?

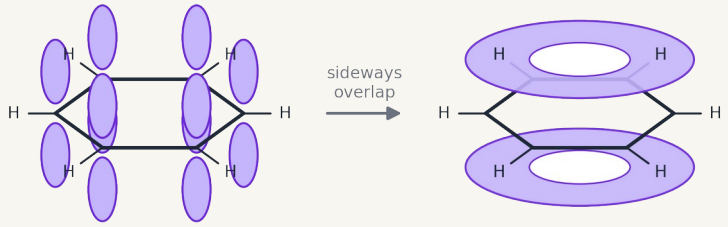
Your answer

delocalisation energy: the _____ 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 _____ 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?

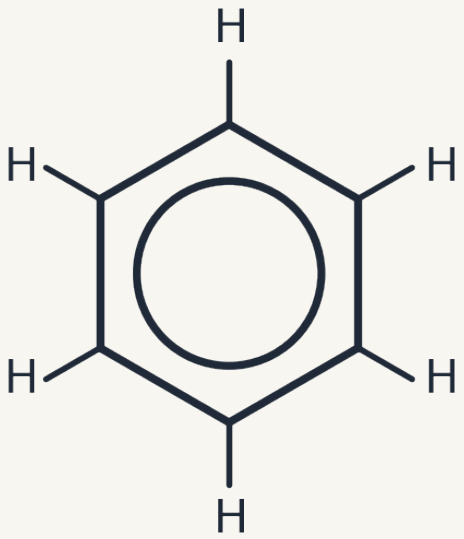
Your answer

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

Question

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

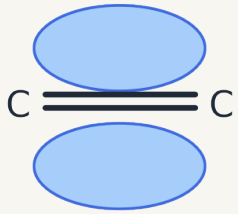
Your answer

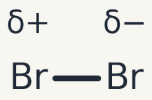
Why won't benzene react with bromine? (spec f)

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

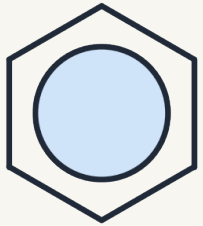




dipole induced → electrophile

alkene: reacts (electrophilic addition)

delocalised π system
= LOWER electron density
between any two carbons



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

Your answer

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.

Draw it here after the whiteboard check

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.

Your answer

2 [3 marks]

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

Your answer

3 [2 marks]

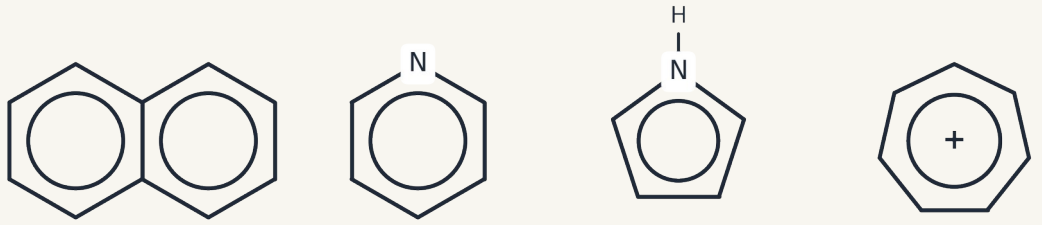
Why does benzene not decolourise bromine water?

Your answer

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?

Your answer

Lesson 2

2 Naming aromatic compounds

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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 $CH_3CHClCH_3$.

Your answer

2

Name $CH_3CH(OH)CH_3$.

Your answer

3

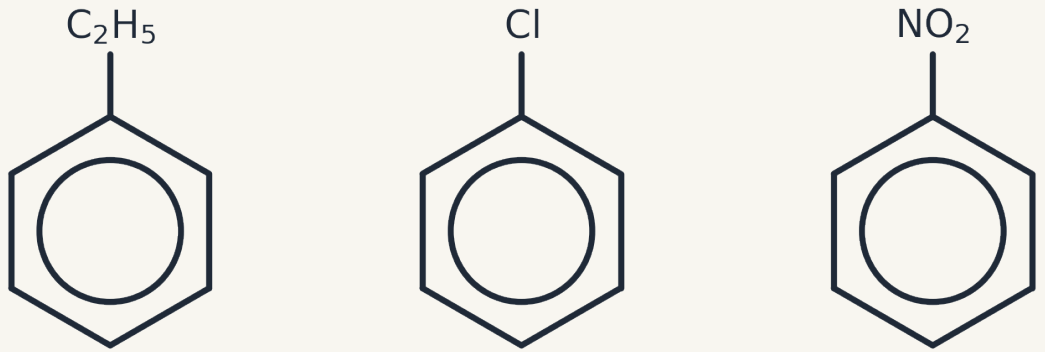
What is the empirical formula of benzene, C_6H_6?

Your answer

Rule 1: one group — prefix + benzene

Lesson 2

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



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

Question

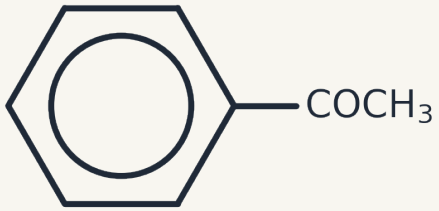
Name the three compounds shown.

Your answer

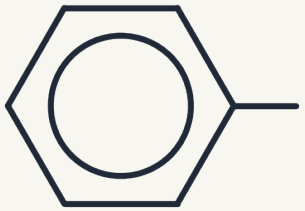
Rule 2: when the ring is the add-on — 'phenyl'

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 _____, or to a chain of _____ or more carbons, the ring becomes a substituent called _____ (C_6H_5–).

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

Question

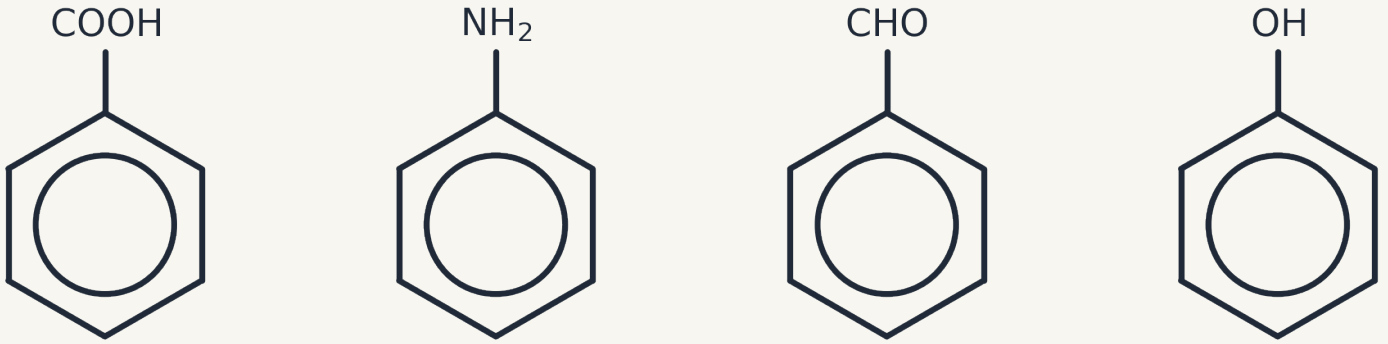
Why is $C_6H_5COCH_3$ called phenylethanone, not 'ethanoylbenzene'?

Your answer

Rule 3: four names to LEARN

Lesson 2

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



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

Question

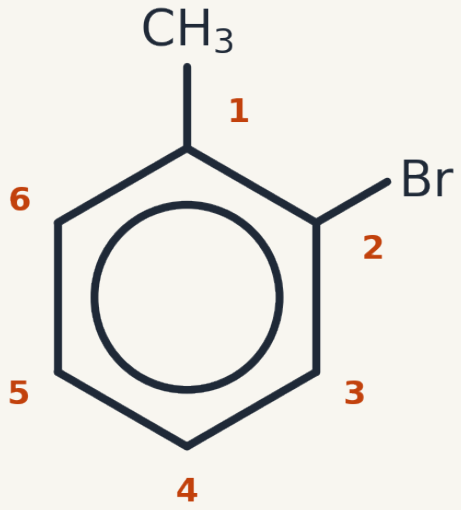
Name A–D. Which one would fizz with sodium carbonate? Which one is a base?

Your answer

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 _____).

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

Step 3: write prefixes in _____ order.

Question

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

Your answer

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

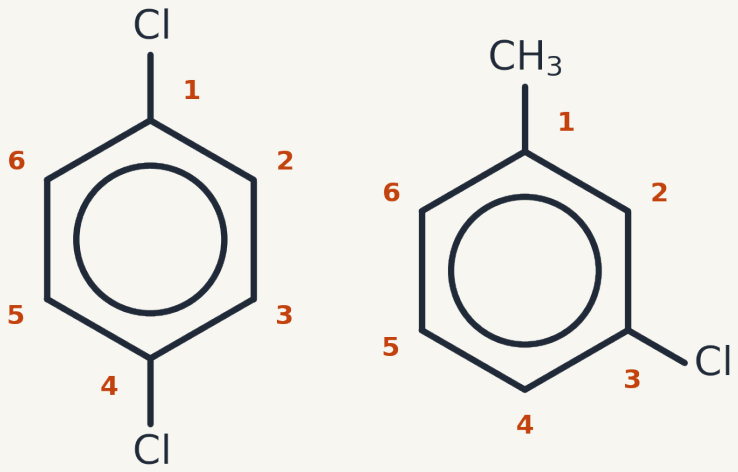
1 **Core** questions 1–3

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

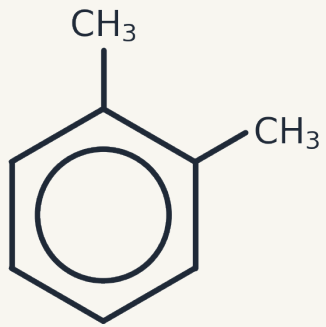
Name each compound. Check: lowest numbers? Alphabetical order?

Your answer

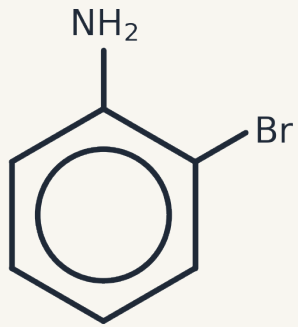
Your turn: name these

Lesson 2

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

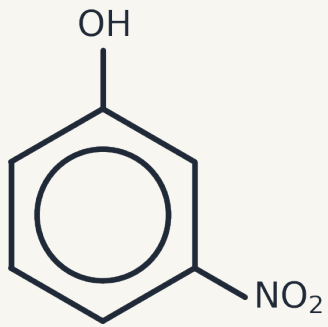


A



B

C



D

Question

Name compounds A–D.

Your answer

Your turn: draw these

Lesson 2

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

Draw your answer here

Question

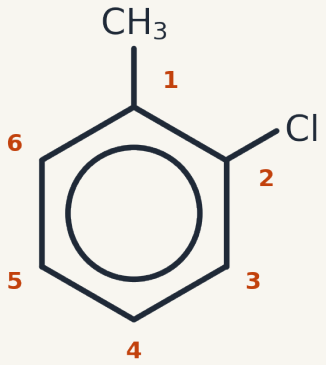
Draw the skeletal formula of: (a) 1,3-dinitrobenzene (b) 2,4,6-trichloromethylbenzene (c) 2,3-dichlorobenzoic acid (d) phenylpropanone (e) 1,2,4-tribromobenzene

Your answer

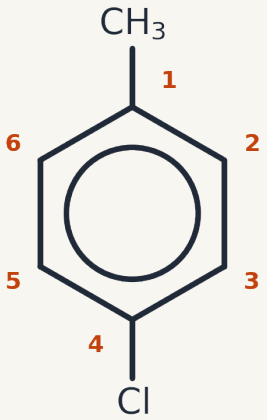
Spot the mistake

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?

Your answer

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 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 $C_6H_5CH_2CH_3$.

Your answer

2 [1 mark]

Draw 2,4-dinitromethylbenzene.

Your answer

3 [1 mark]

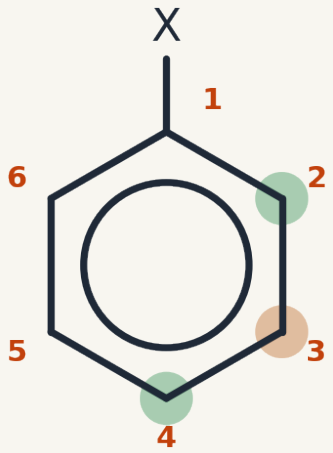
A compound has a benzene ring with –OH on carbon 1 and –Cl on carbons 2 and 4. Give its systematic name.

Your answer

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?

Your answer

Lesson 3

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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'.

Your answer

2

What does a curly arrow show?

Your answer

3

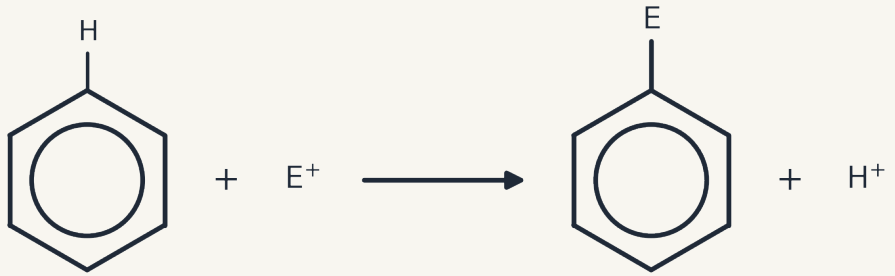
Why does benzene not undergo addition reactions easily?

Your answer

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 _____ by the electrophile.

The stable delocalised ring is _____.

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

Question

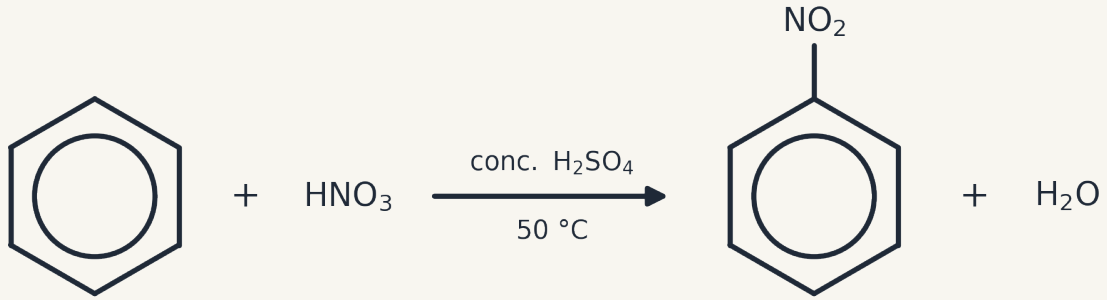
Why does benzene 'prefer' substitution to addition?

Your answer

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



benzene nitrobenzene

Reagents: _____ + _____ (catalyst).
Conditions: _____ °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?

Your answer

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, _____.

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

Question

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

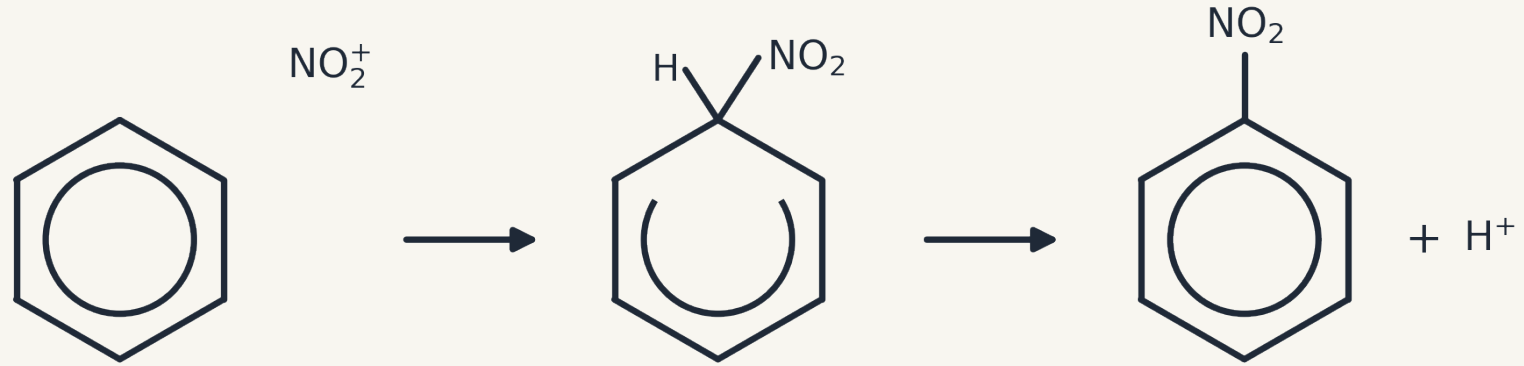
nitronium ion: NO_2^+ — the electrophile in nitration

Your answer

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

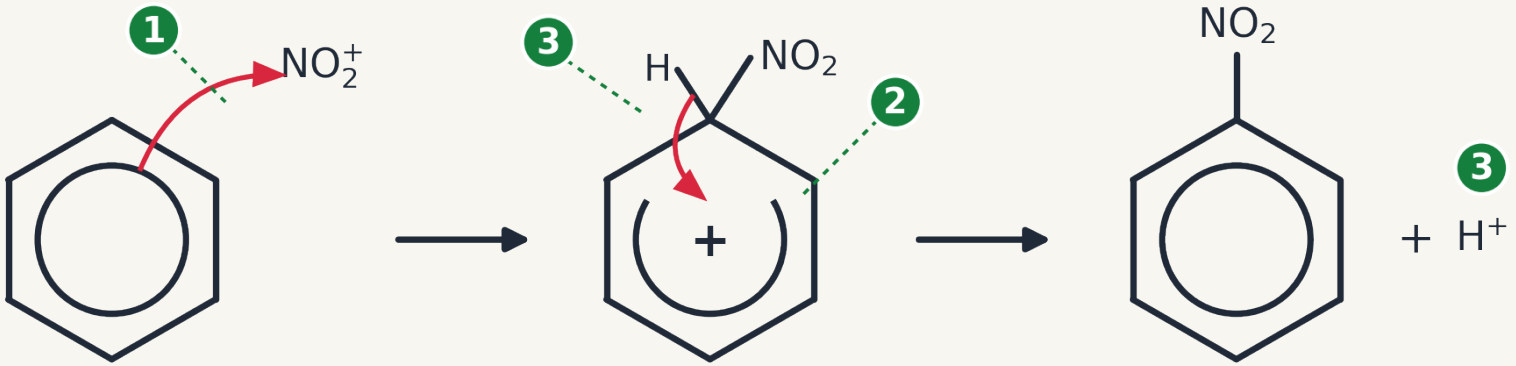
Where must the FIRST curly arrow start, and where must it finish?

Your answer

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 _____ (the electron pair), head _____ the N of NO_2^+ — never an O.

② Intermediate: _____ stopping either side of the carbon that holds the H and NO_2; + _____ it; H and NO_2 on the _____.

③ Arrow 2: tail on the _____ (never the H), head _____ towards the +. Products: nitrobenzene + H^+.

Question

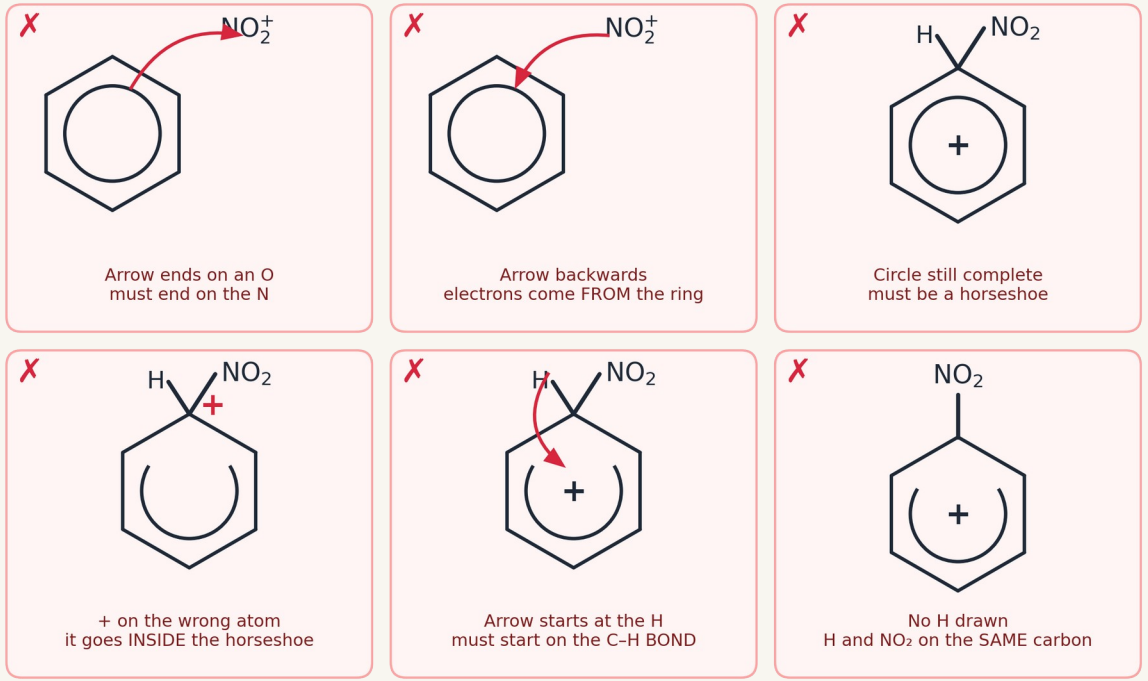
A 'show the role of the catalyst' mechanism question is worth 5 marks. Where are the other two?

Your answer

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.

Your answer

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.

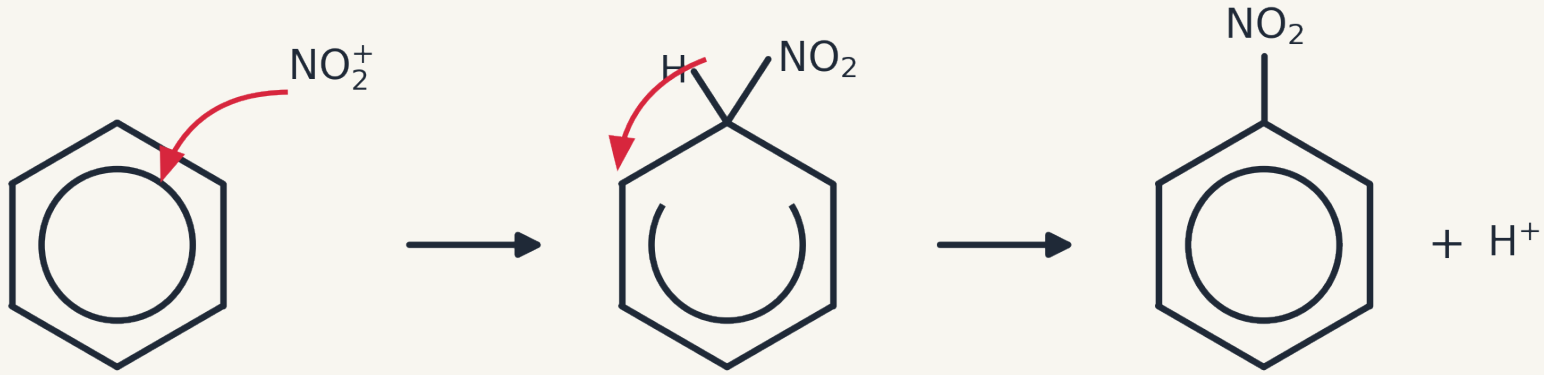
catalyst: speeds up a reaction and is regenerated — not used up overall

Your answer

Exam skills: mark this mechanism

Lesson 3

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



benzene intermediate

Question

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

Your answer

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

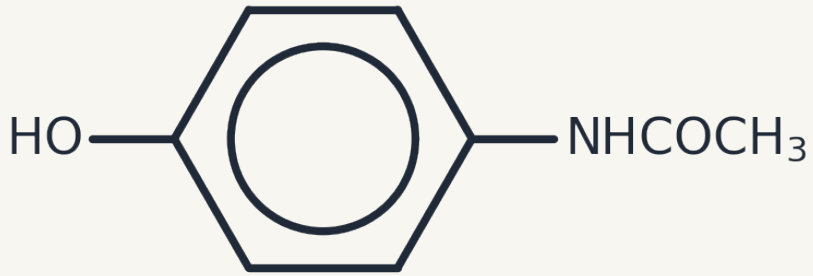
1. **Core** questions 5–8
2. **Then** Exam-style E1 — in class, in silence, in one go
3. **Finished?** Harder H1–H4 — same ideas, more to think about
4. **Finished those?** Uni worksheet U3 The Wheland intermediate (purple, not examined)

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 _____.

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?

Your answer

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.

Your answer

2 [3 marks]

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

Your answer

3 [2 marks]

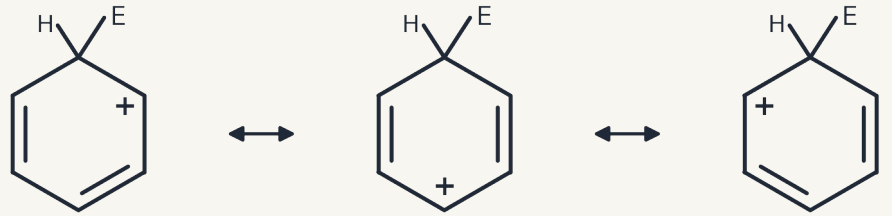
State the conditions for nitration and explain the role of H_2SO_4.

Your answer

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?

Your answer

4

Lesson 4

STUDENT COPY

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.

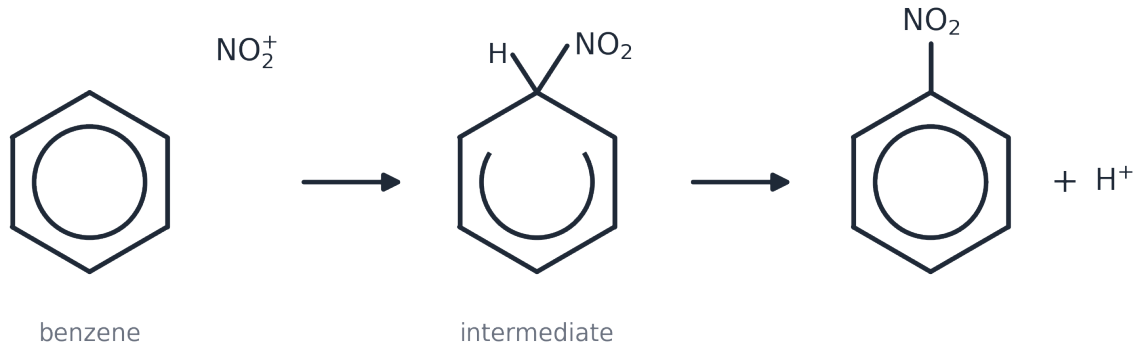
2

Write the equation for the formation of NO_2^+.

3

What does 'delocalised' mean?

Complete the mechanism



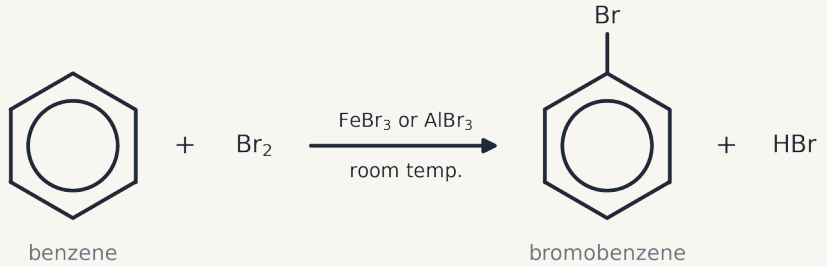
Your answer

Your answer

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 _____ catalyst is present: $FeBr_3$, $AlBr_3$, $AlCl_3$, $FeCl_3$ or _____ 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.)

Your answer

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 _____ ion. (The spec lets you assume the electrophile is X^+.)

Question

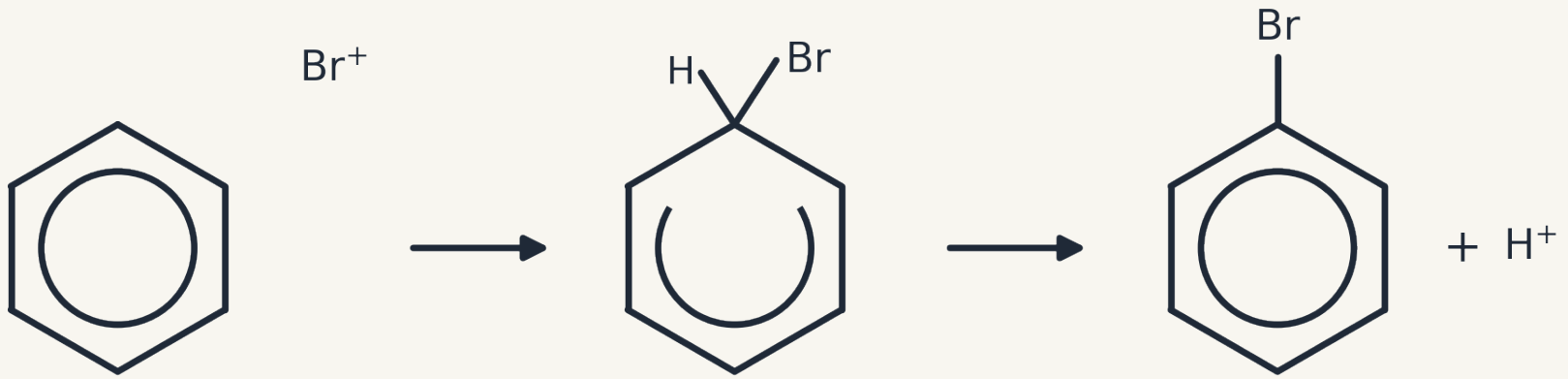
What is $FeBr_3$ doing to the Br_2 molecule? Think about electron pairs.

Your answer

Step 2: the mechanism — same pattern!

Lesson 4

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



benzene intermediate

Question

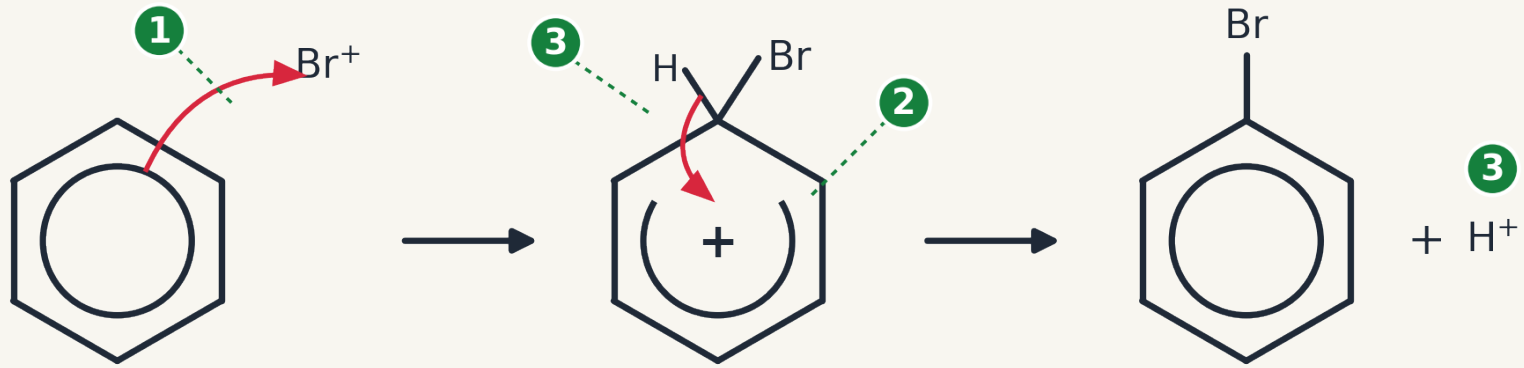
Compare this with nitration. What is the SAME? What is DIFFERENT?

Your answer

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 _____ (the electron pair), head _____ Br^+.

② Intermediate: _____ stopping either side of the carbon that holds the H and Br; + _____ it; H and Br on the _____.

③ Arrow 2: tail on the _____ (never the H), head _____ towards the +. Products: bromobenzene + H^+.

Question

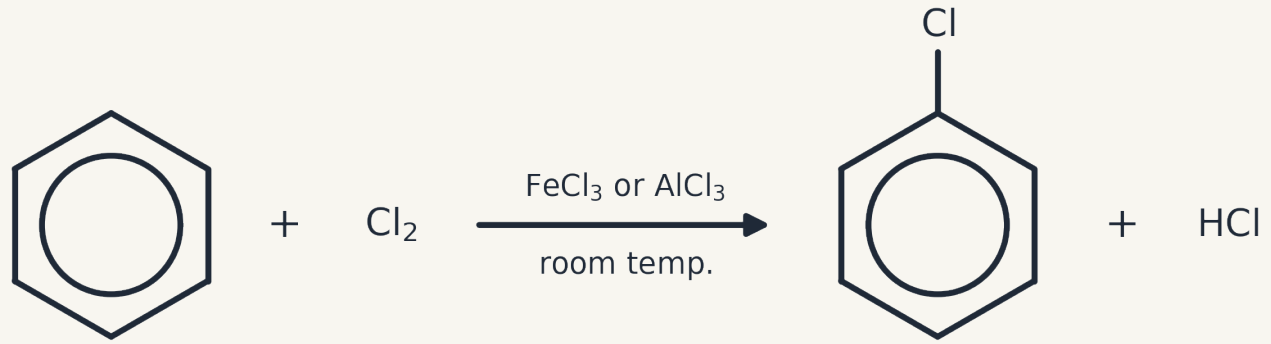
Two more marks are on offer in a halogenation question. Write the two equations that earn them.

Your answer

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.

Your answer

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

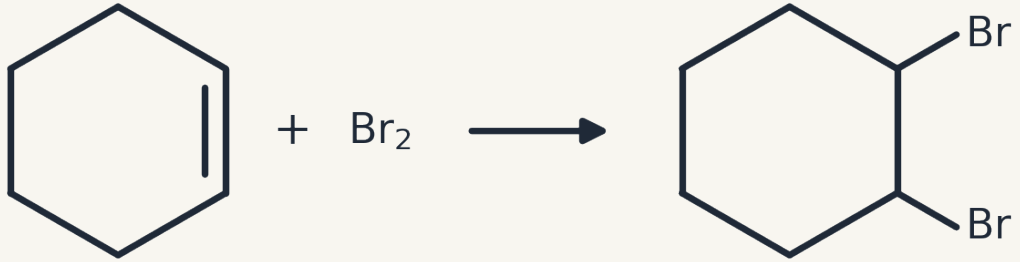
1 **Core** questions 1–4

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

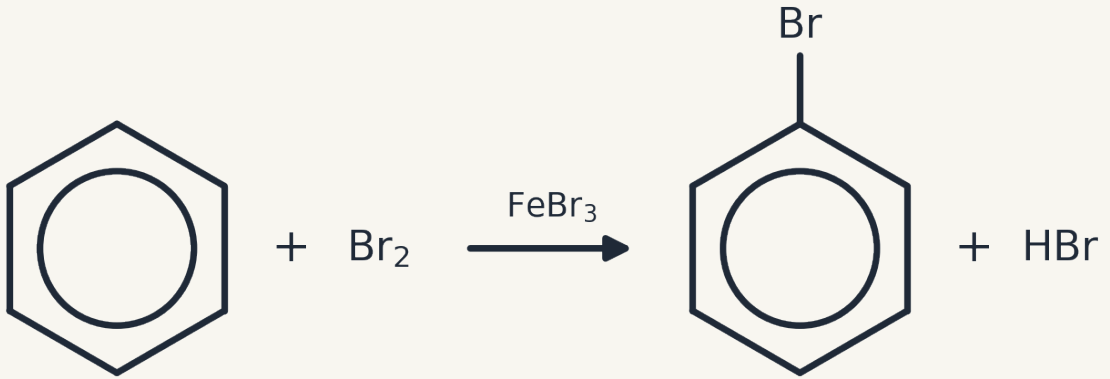
Alkene vs arene with bromine

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

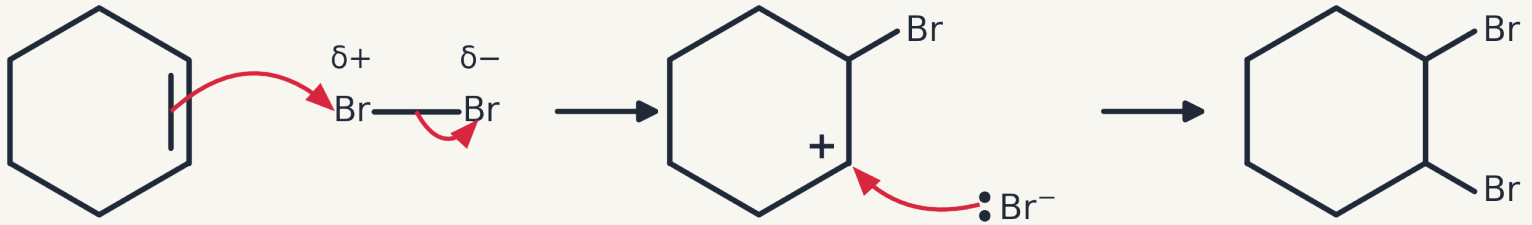
Copy and complete the comparison table.

	Cyclohexene	Benzene
Type of reaction	electrophilic addition	
Catalyst?	none needed	
Observation	orange → colourless	
Product(s)	1,2-dibromocyclohexane	

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 _____ to the δ+ Br · 2 from the _____ to the δ− Br · 3 from the _____ to the C^+.

Question

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

Your answer

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.

Draw it here after the whiteboard check

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 $FeBr_3$.

Your answer

2 [4 marks]

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

Your answer

3 [3 marks]

Explain why benzene is less reactive with bromine than cyclohexene.

Your answer

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?

Your answer

Lesson 5

STUDENT COPY

5 Friedel–Crafts: building C–C bonds

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?

Your answer

2

Draw the intermediate in the bromination of benzene.

Your answer

3

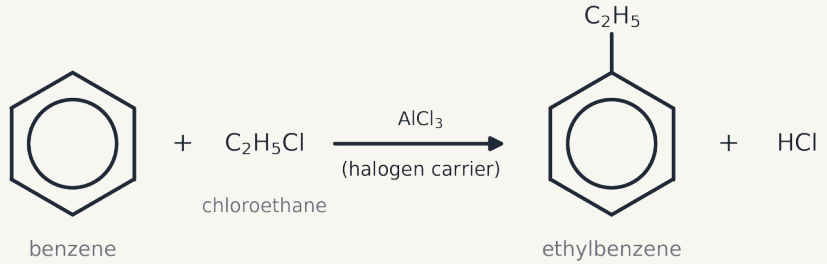
Name $C_6H_5COCH_3$.

Your answer

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 _____ bond to the ring.

Reagents: a _____ or an _____ + 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?

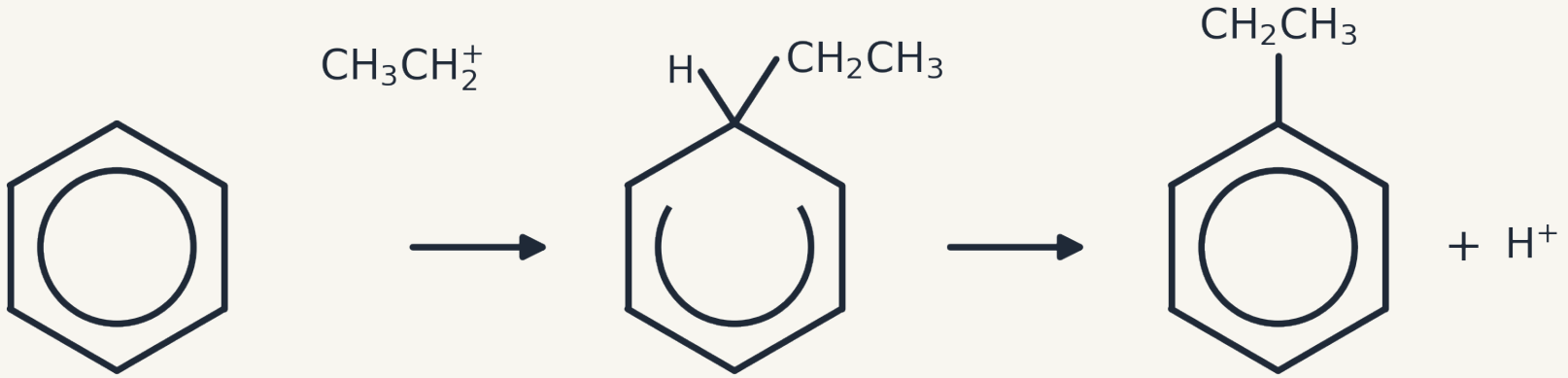
Your answer

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

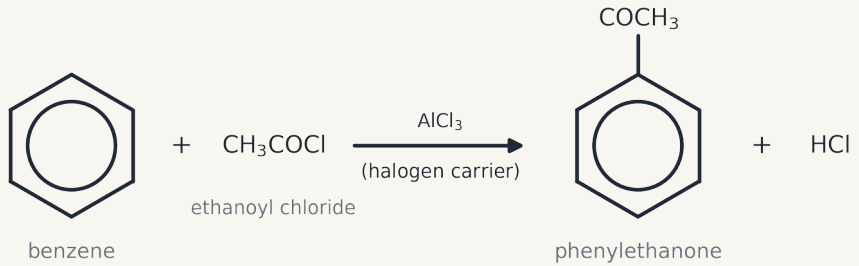
Write the three steps (make the electrophile; substitution; regenerate the catalyst) for the alkylation of benzene with chloroethane.

Your answer

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 _____.

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

The electrophile is the acylium ion, CH_3CO^+.

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

Question

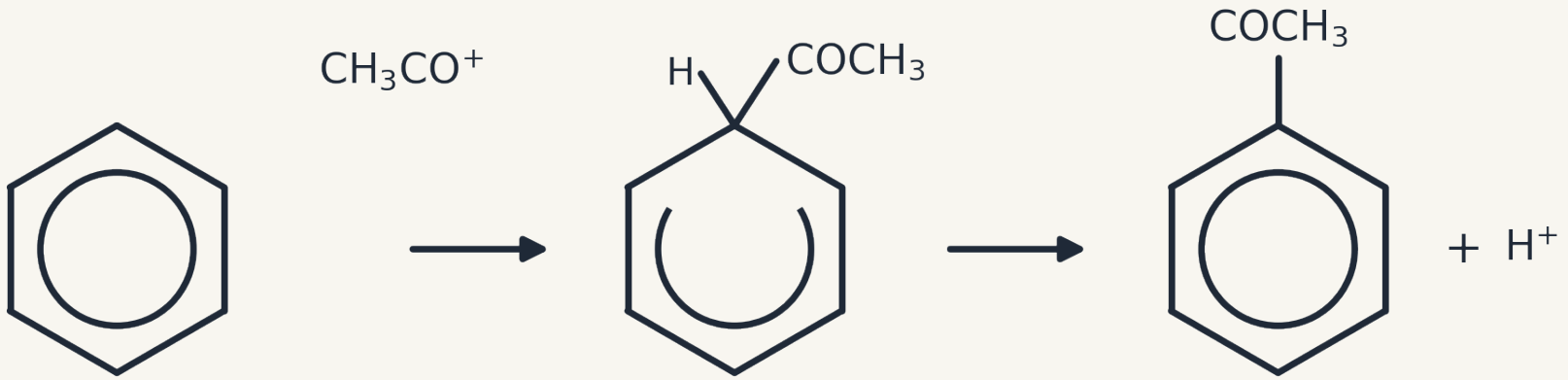
Write the equation for the formation of the electrophile from CH_3COCl and $AlCl_3$.

Your answer

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

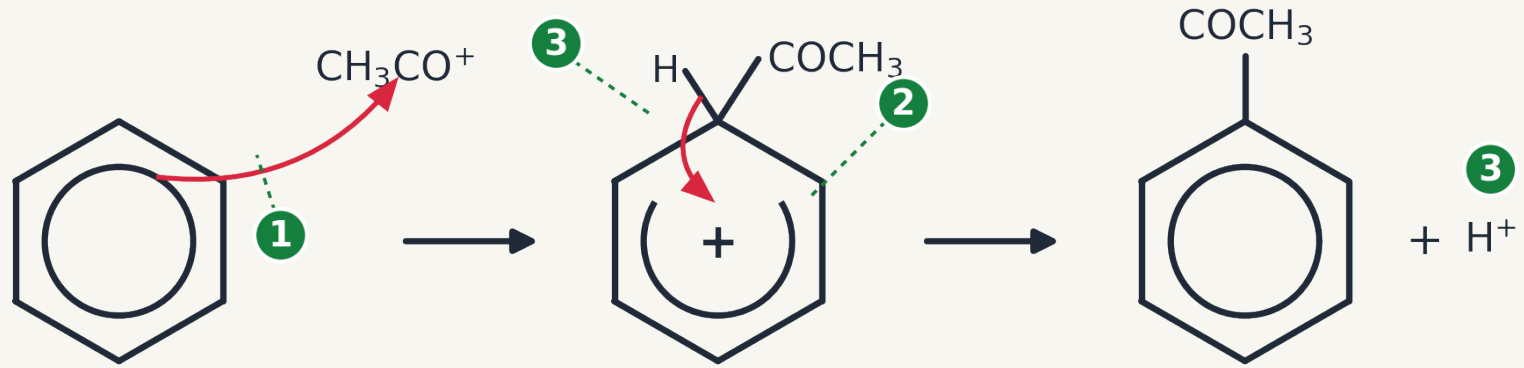
Draw the mechanism for the acylation of benzene with CH_3CO^+ — same pattern!

Your answer

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 _____ (the electron pair), head _____ the C=O carbon of CH_3CO^+ — the one with the +.

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

③ Arrow 2: tail on the _____ (never the H), head _____ towards the +. Products: phenylethanone + H^+.

Question

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

Your answer

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

Draw your answer here

Question

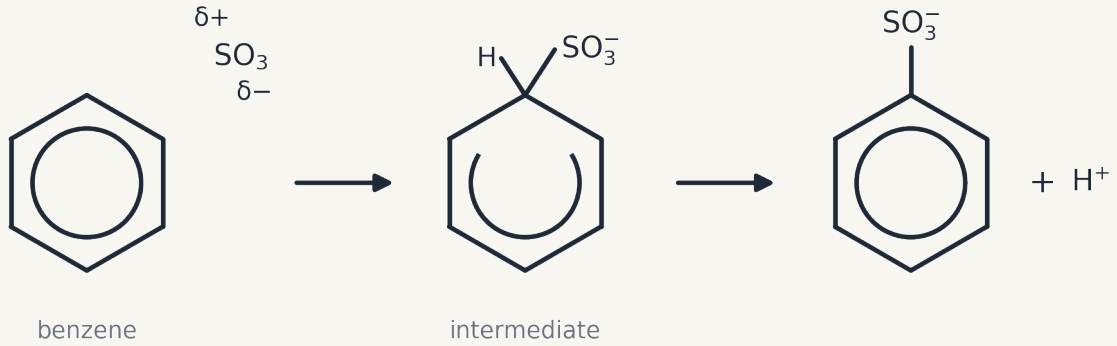
Predict the organic product when benzene reacts, with $AlCl_3$, with: A $(CH_3)_2CHCOCl$ B C_6H_5COCl C 2-chloropropane, $CH_3CHClCH_3$

Your answer

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

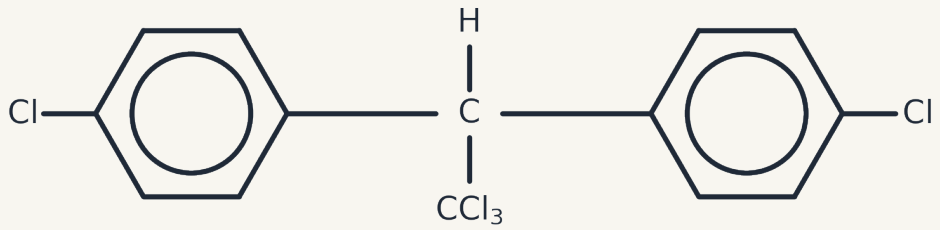
Complete the mechanism. Which atom does the ring attack? Where does the + charge go? What happens to the product ion?

Your answer

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.

Your answer

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 $AlCl_3$.

Your answer

2 [2 marks]

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

Your answer

3 [1 mark]

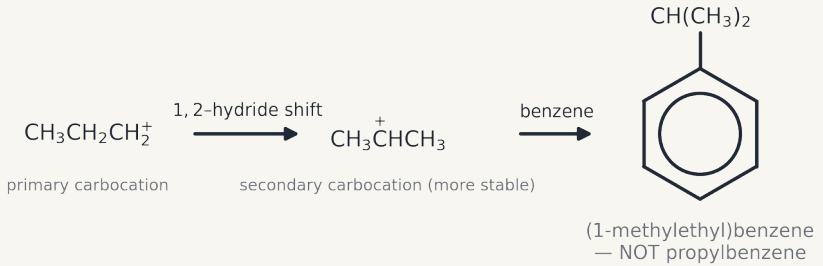
Why are Friedel–Crafts reactions important in organic synthesis?

Your answer

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?

Your answer

Lesson 6

6 Phenol

STUDENT 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?

Your answer

2

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

Your answer

3

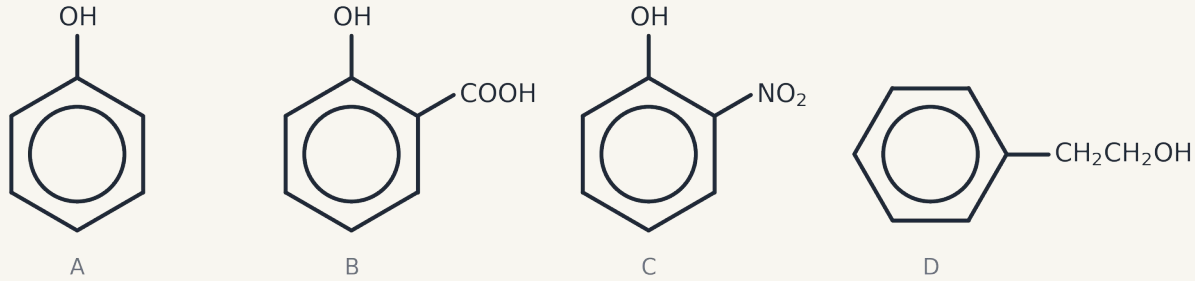
Name C_6H_5OH.

Your answer

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



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

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

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

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

Question

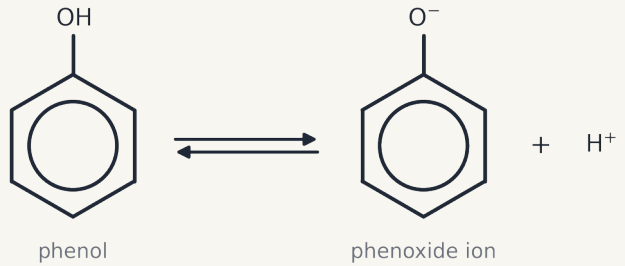
Which of A–D is NOT a phenol?
How can you tell?

Your answer

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).

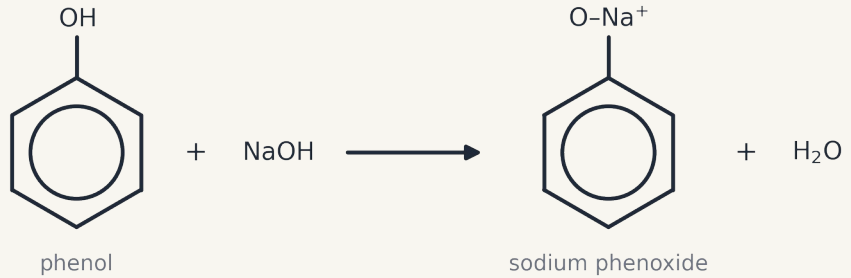
Compound	K_a at 298 K / mol dm^{-3}	Order
ethanol	1.0×10^{-16}	
phenol	1.3×10^{-10}	
ethanoic acid	1.7×10^{-5}	

Your answer

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 → _____: phenol is too weak an acid to release CO_2 from a carbonate.

Carboxylic acids DO react with carbonates.

Question

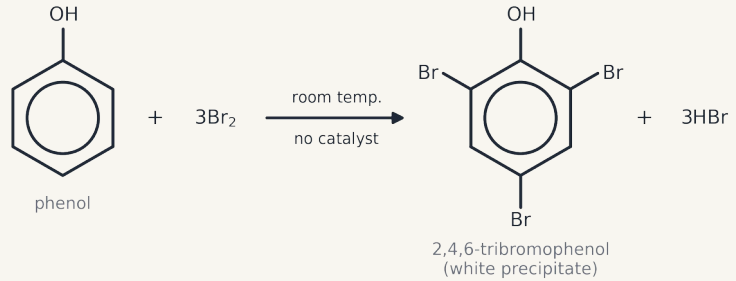
You have two unlabelled bottles of white solid: phenol and benzoic acid. Describe a simple test to tell them apart.

Your answer

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 _____ and a _____ of 2,4,6-tribromophenol forms.

Question

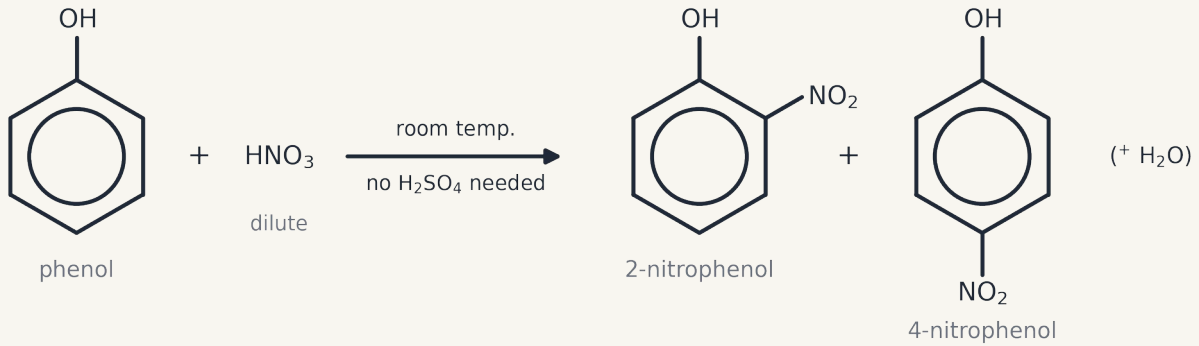
List THREE differences between the bromination of phenol and the bromination of benzene.

Your answer

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 — 2-nitrophenol — 4-nitrophenol

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

Products: a mixture of _____ and _____.

Question

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

Your answer

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

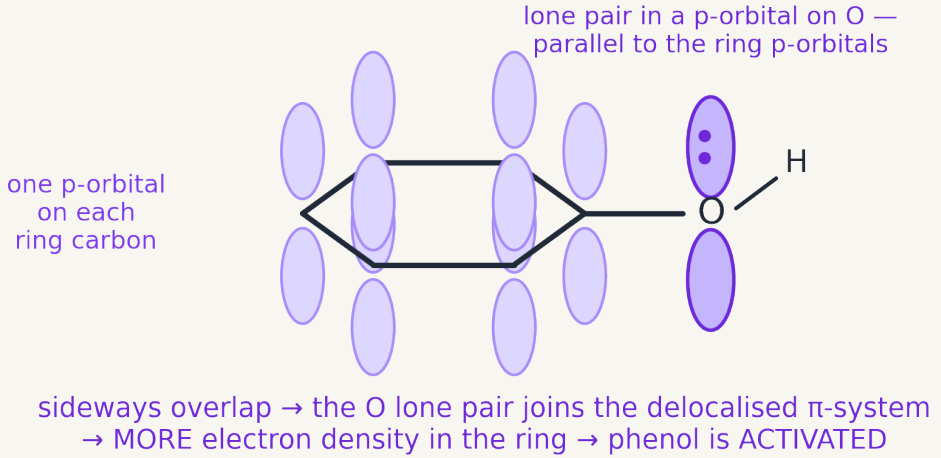
1 **Core** questions 1–3 and 6–7

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

One _____ on the oxygen is in a _____ 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.

Your answer

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

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		
Catalyst		
Observation		
Product		
Why?		

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.

Your answer

2 [3 marks]

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

Your answer

3 [3 marks]

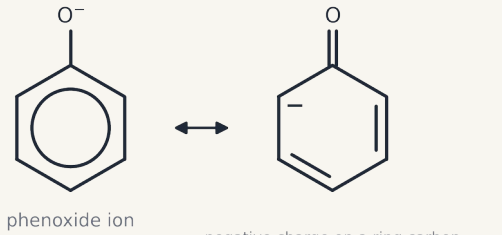
Explain why phenol reacts more readily than benzene with electrophiles.

Your answer

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, $C_6H_5O^-$?

Your answer

7

Lesson 7

STUDENT 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?

Your answer

2

Name the product of phenol + excess bromine water.

Your answer

3

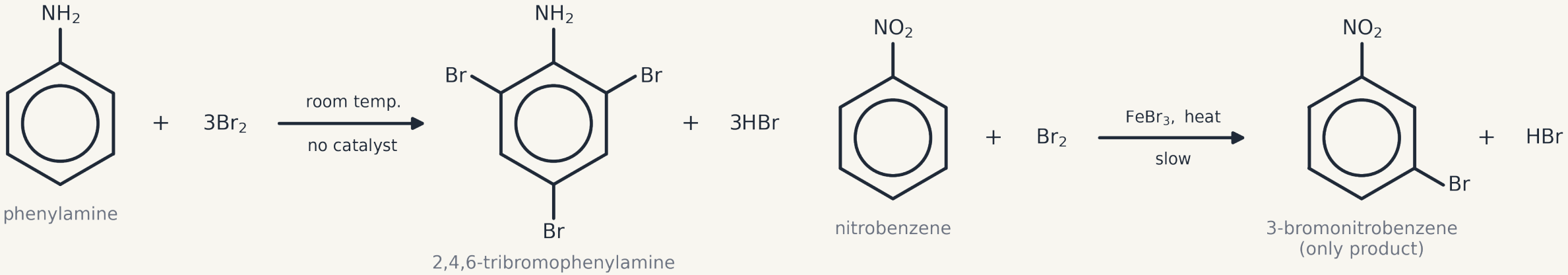
Name $C_6H_5NH_2$.

Your answer

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.

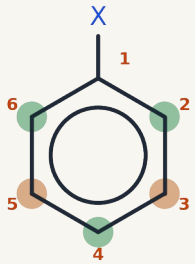
directing group: a group already on the ring that decides where the next group goes

Your answer

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-_____ groups (–OH, –NH_2): activate the ring → direct to positions _____.

Electron-_____ groups (–NO_2): deactivate the ring → direct to position _____.

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'?

Your answer

Predicting products 1

Lesson 7

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

Draw your answer here

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.

Your answer

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

Draw your answer here

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?

Your answer

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

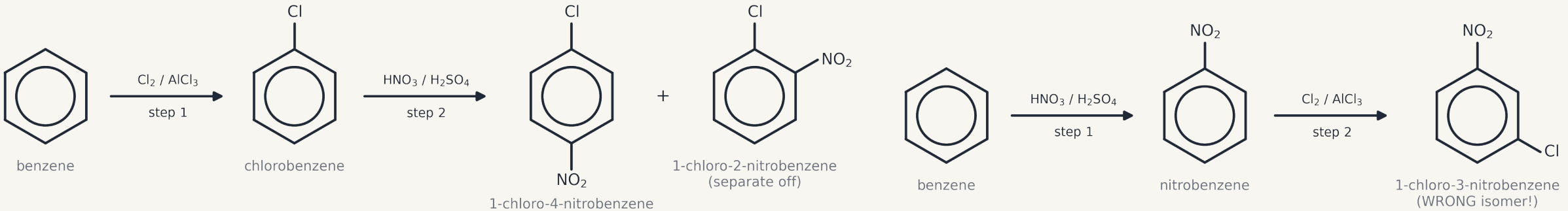
1 **Core** questions 1–2 and 4–5

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?

Your answer

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

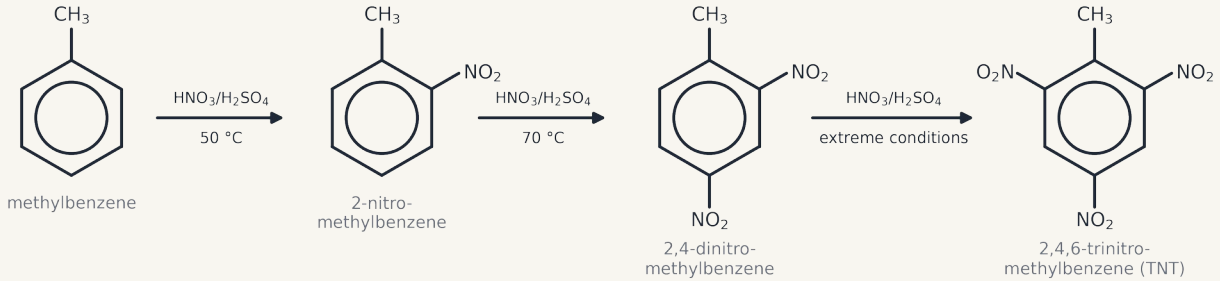
Stretch: In real labs, Friedel–Crafts fails on nitrobenzene (the ring is too deactivated) — route (a) is an A-level answer, not an industrial one. Ask the G&T student how a chemist might really make it.

Your answer

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 _____ 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.

Your answer

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.

Your answer

2 [2 marks]

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

Your answer

3 [2 marks]

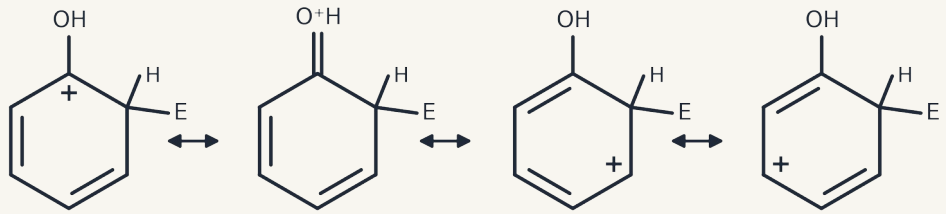
Suggest a two-step synthesis of 1-bromo-4-nitrobenzene from benzene.

Your answer

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.

Your answer

Final section

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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.

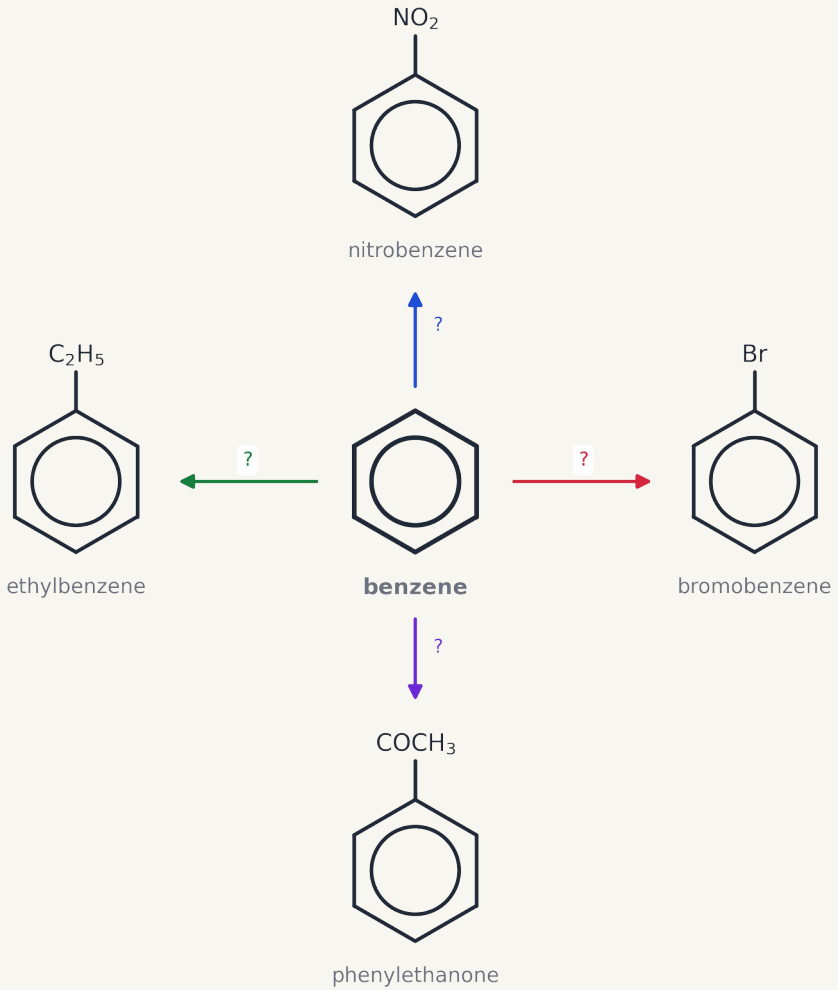
In plain English — by the end of this lesson I can…

- [ ] 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?

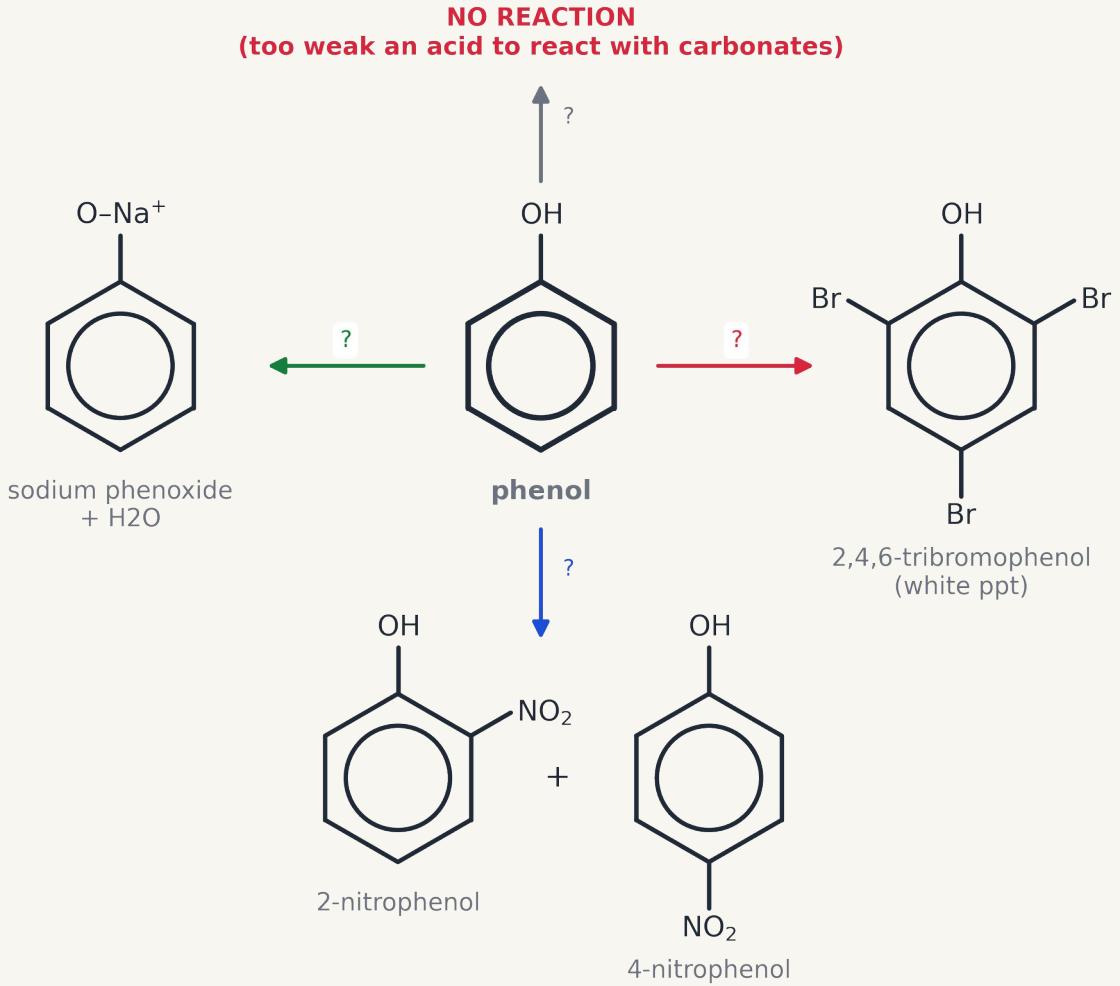
Your answer

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?

Your answer

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

Your answer

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)

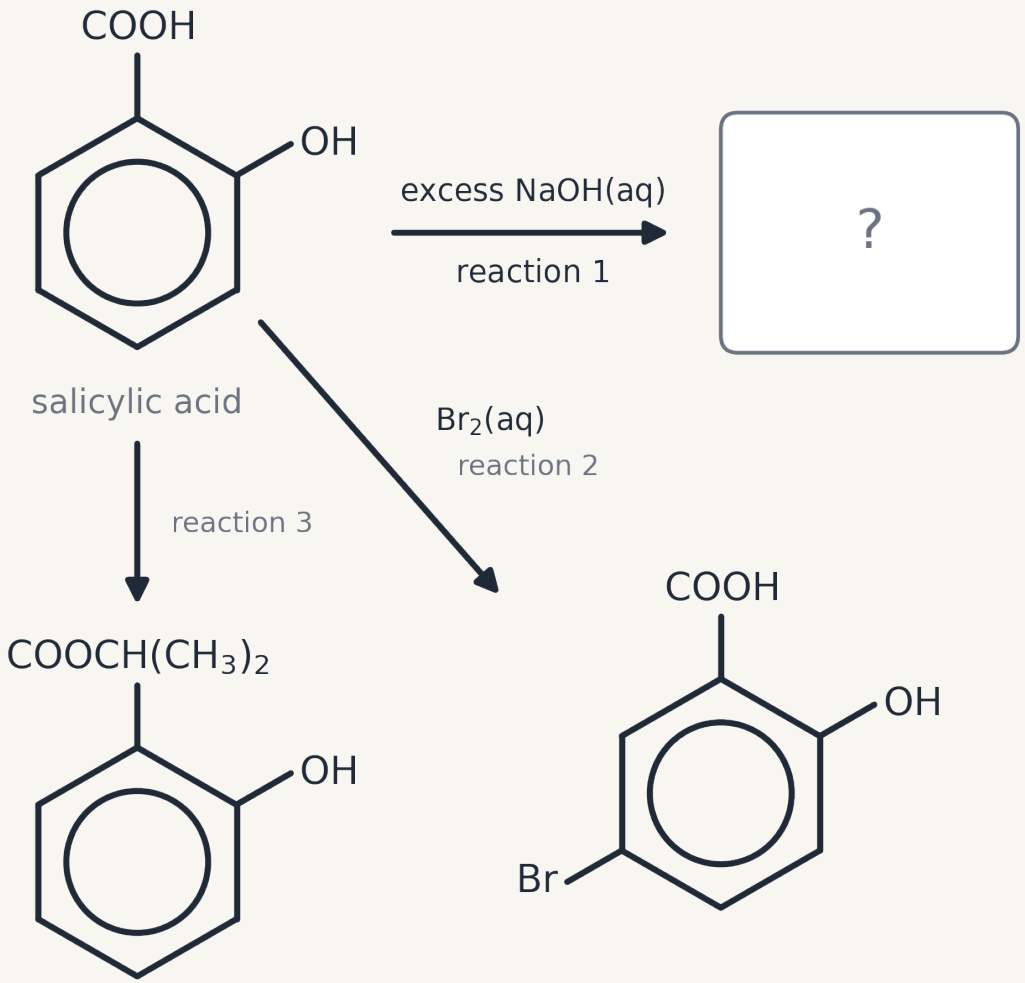
Stuck on a mechanism? Recipe card in the Support Guide. Mark schemes: ANSWERS booklet / Mark your work on the site.

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?

Your answer

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

Draw your answer here

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.

Your answer

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.