

Cambridge AS & A Level · Chemistry 9701 · Notes

Hydroxy compounds

A2

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Read first: [Hydroxy compounds](#), [Hydrocarbons](#)

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What you need to know

At AS you learned the alcohols. At A Level this topic adds one new alcohol reaction and then turns to **phenol**, C_6H_5OH , where the OH group sits directly on a benzene ring. You should be able to:

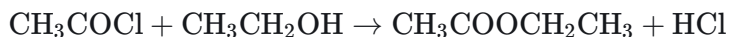
1. **Turn an alcohol into an ester with an acyl chloride.** For example, ethanol and ethanoyl chloride give ethyl ethanoate and hydrogen chloride, quickly and at room temperature.
2. **Make phenol from phenylamine in two stages:** first a diazonium salt, made cold (below 10 °C) from nitrous acid, then warming that salt in water.
3. **Know five reactions of phenol**, with the reagents and conditions for each: with sodium hydroxide solution and with sodium metal (both give sodium phenoxide; sodium also gives hydrogen gas), with a diazonium salt in alkali (an azo dye), with dilute nitric acid at room temperature (2-nitrophenol and 4-nitrophenol), and with bromine water (2,4,6-tribromophenol).
4. **Say why phenol is an acid**, and put water, phenol and ethanol in order of acidity with reasons.
5. **Explain why phenol needs gentler conditions than benzene** for bromination and for nitration.
6. **Know where new groups go:** the OH group of a phenol sends them to positions 2, 4 and 6 of the ring.
7. **Use the same chemistry on other phenols**, such as naphthols, methylphenols or larger molecules that contain a phenol group.

Exam questions on this topic nearly always compare phenol's acidity with carboxylic acids (topic 33) and alcohols, and put a phenol group inside a bigger molecule, so those comparisons are included here. The mechanism of electrophilic substitution belongs to "Hydrocarbons" and the reactions of alcohols to AS "Hydroxy compounds"; both are only recapped.

Understand it

Alcohols and acyl chlorides

An acyl chloride, $RCOCl$, has a carbon bonded to both an oxygen and a chlorine. Both pull electrons away, so that carbon is strongly $\delta+$. The oxygen of an alcohol has lone pairs, so it acts as a **nucleophile** and attacks that carbon. The overall reaction swaps Cl for the alcohol's OR group:



It happens at room temperature, needs no catalyst, is fast and goes to completion, and steamy fumes of HCl are given off. Making the same ester from ethanoic acid needs a concentrated sulfuric acid catalyst, heating, and only reaches an equilibrium. The ester is named from the alcohol first, then the acid part: **ethyl** (from ethanol) **ethanoate** (from the ethanoyl group).

The mechanism is **nucleophilic addition–elimination**:

1. A lone pair on the alcohol's oxygen forms a bond to the δ^+ carbon of $\text{C}=\text{O}$. At the same time the π electrons of $\text{C}=\text{O}$ move onto the oxygen (show the dipole $\text{C}^{\delta+}=\text{O}^{\delta-}$ and both curly arrows).
2. This gives an **intermediate** with four groups on the carbon: O^- , Cl, R and the alcohol's oxygen, which now carries a + charge and still has its H.
3. The O^- lone pair moves back to reform $\text{C}=\text{O}$, and the $\text{C}-\text{Cl}$ bond breaks so that Cl^- leaves (two curly arrows). The H^+ is then lost from the positive oxygen and joins Cl^- as HCl.

Phenols form esters with acyl chlorides in the same way (warming may help), but they react only very poorly with carboxylic acids, so an acyl chloride is the way to make a phenyl ester.

Why phenol is an acid

An acid gives away H^+ . For any OH compound, $\text{ROH} \rightleftharpoons \text{RO}^- + \text{H}^+$. It is a stronger acid when the O–H bond is **weaker** (the H^+ comes off more easily) or when the negative ion left behind, the **conjugate base**, is **more stable**.

In phenol the oxygen is joined to a ring carbon. One of its lone pairs sits in a p orbital that lies parallel to the ring's p orbitals, so it **overlaps with the delocalised π system**. Two things follow:

- in phenol, electron density is drawn from the O–H bond into the ring, which weakens the bond;
- in the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$, the negative charge is spread over the ring instead of sitting on one oxygen, so the ion is stabilised.

So phenol loses H^+ more easily than water does: it is a weak acid, more acidic than water. In ethanol the opposite happens. The ethyl group **donates electrons** (positive inductive effect), which strengthens the O–H bond and concentrates the negative charge on the O of the ethoxide ion, so ethanol is a slightly weaker acid than water.

A carboxylic acid is stronger still. Its OH is next to $\text{C}=\text{O}$, which **withdraws electrons** (negative inductive effect), and in the carboxylate ion the charge is shared equally between **two** electronegative oxygen atoms.

	Na	NaOH	Na ₂ CO ₃
↑ more acidic			
carboxylic acid, RCOOH C=O withdraws electrons; charge of RCOO ⁻ shared by two O atoms	yes	yes	yes
phenol, C ₆ H ₅ OH O lone pair delocalised into ring; charge of C ₆ H ₅ O ⁻ spread over ring	yes	yes	no
water, H ₂ O the reference	yes	–	–
alcohol, ROH alkyl group donates electrons; charge of RO ⁻ stays on one O	yes	no	no

The same ideas rank any set of OH compounds:

- **Groups that withdraw electrons** (Cl, NO₂, C=O) make the O–H weaker and the anion more stable: the compound is **more** acidic.
- **Groups that donate electrons** (alkyl groups, including a CH₂ joining an OH to a ring) make it **less** acidic. ArCH₂OH compounds (Ar = a benzene ring) are alcohols, not phenols: the CH₂ stops the lone pair reaching the ring.

The order of acidity shows up in what each compound reacts with. Phenol reacts with sodium, and with sodium hydroxide solution (a neutralisation):

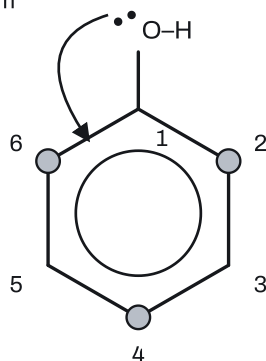


But phenol is too weak an acid to release CO₂ from sodium carbonate, which a carboxylic acid does. Alcohols react with sodium but not with NaOH(aq).

Why phenol's ring is so reactive

The same lone-pair overlap that makes phenol acidic also **increases the electron density of the ring**, most of all at the carbons in positions 2, 4 and 6 (counting the carbon holding OH as 1). A more electron-rich ring attracts electrophiles more strongly, and it can **polarise** a molecule such as Br₂ by itself. Phenol therefore does electrophilic substitution far more easily than benzene, and the new groups go to positions 2, 4 and 6: the OH group is **2,4,6-directing** (also called 2,4-directing).

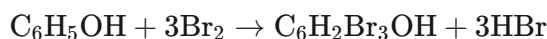
O lone pair overlaps with the ring π system



shaded: positions 2, 4, 6
electron-rich:
electrophiles attack here

Reaction	Benzene	Phenol
Bromination	Br_2 with an AlBr_3 (or FeBr_3) catalyst	Bromine water, $\text{Br}_2(\text{aq})$, room temperature, no catalyst
Product	Bromobenzene (one Br)	2,4,6-tribromophenol (three Br) and 3HBr
Nitration	Concentrated HNO_3 and concentrated H_2SO_4 , about 50°C	Dilute $\text{HNO}_3(\text{aq})$, room temperature
Product	Nitrobenzene	A mixture of 2-nitrophenol and 4-nitrophenol

With bromine water the orange colour disappears at once and a **white precipitate** of 2,4,6-tribromophenol forms:

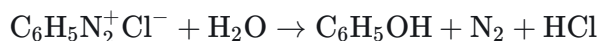


Nitration with dilute acid adds one NO_2 group, at position 2 or position 4, giving two isomers of $\text{C}_6\text{H}_5\text{NO}_3$ ($M_r = 139$). Position 6 is the same as position 2, so there are only two products.

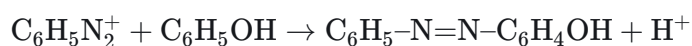
Making phenol and azo dyes

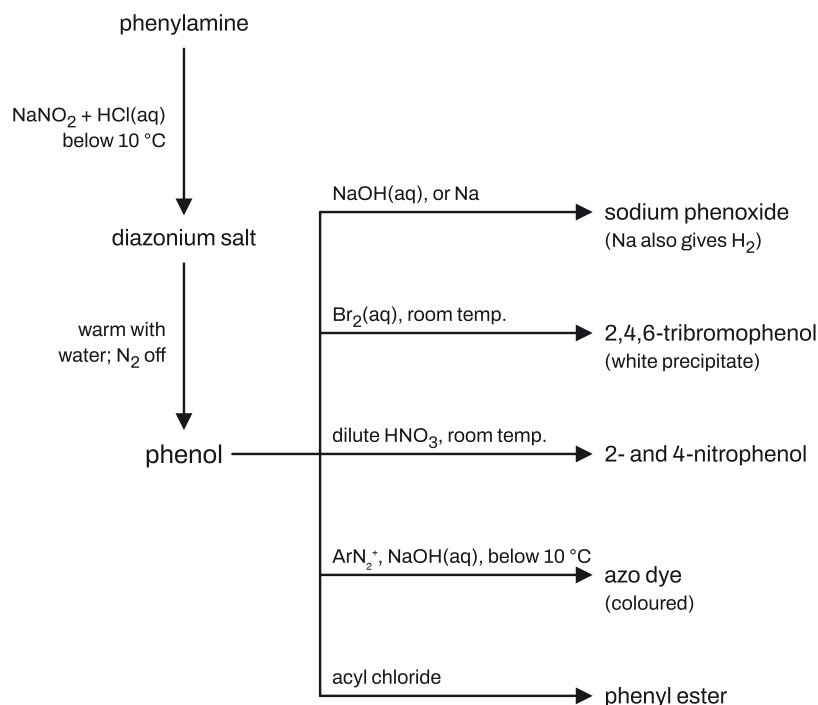
Phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, is turned into phenol through a **diazonium salt**:

- 1. Diazotisation.** Add sodium nitrite and dilute hydrochloric acid (together they make nitrous acid, HNO_2) and keep the mixture **below 10°C** . This gives benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$. The + charge is on the nitrogen joined to the ring.
- 2. Warm with water** (above 10°C). The diazonium ion breaks up, giving off nitrogen gas:



Diazonium salts are unstable, which is why step 1 must be cold. If the diazonium salt is instead kept cold and added to a phenol **dissolved in $\text{NaOH}(\text{aq})$** , the two join through an $-\text{N}=\text{N}-$ bridge, the **azo group**, usually at position 4 of the phenol. The product is a brightly coloured **azo dye** (yellow, orange or red), and the reaction is called **coupling**. The alkali turns the phenol into the phenoxide ion, whose ring is even more electron-rich.





Other phenols

Any compound with an OH directly on an aromatic ring behaves like phenol: it reacts with Na and NaOH(aq) (not Na_2CO_3), decolourises bromine water, nitrates with dilute nitric acid, and couples with diazonium salts.

Naphthols (an OH on the two fused rings of naphthalene) are the syllabus example. Naphthalen-2-ol couples at carbon 1, next to the OH, giving a red-orange dye.

To predict a product, count the **free** 2, 4 and 6 positions relative to the OH. A group that is already on one of them blocks it: if position 4 is taken, bromine water adds only two Br atoms, at 2 and 6. Other groups in the molecule keep their own chemistry: an alcohol group reacts with Na but not NaOH ; a carboxylic acid group reacts with Na, NaOH and Na_2CO_3 .

Key facts and formulas

"Given" means it is printed on the Periodic Table or in the Data Booklet in the exam. "Learn it" means you must remember it; reagents, conditions, colours and explanations are never printed.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, Na 23.0, Cl 35.5, Br 79.9	Given
Molar volume of gas at room conditions = $24.0\text{ dm}^3\text{ mol}^{-1}$	Given
$\text{ROH} + \text{R}'\text{COCl} \rightarrow \text{R}'\text{COOR} + \text{HCl}$: room temperature, nucleophilic addition–elimination	Learn it

Formula	Status
Phenylamine $\xrightarrow{\text{NaNO}_2 + \text{HCl(aq)}, <10^\circ\text{C}}$ diazonium salt $\xrightarrow{\text{warm with H}_2\text{O}}$ phenol + N ₂	Learn it
$2\text{C}_6\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2\text{C}_6\text{H}_5\text{ONa} + \text{H}_2$; $\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$	Learn it
Phenol + Na ₂ CO ₃ (aq): no reaction	Learn it
$\text{C}_6\text{H}_5\text{OH} + 3\text{Br}_2 \rightarrow \text{C}_6\text{H}_2\text{Br}_3\text{OH} + 3\text{HBr}$: bromine water, room temperature, white precipitate	Learn it
Dilute HNO ₃ , room temperature → 2-nitrophenol + 4-nitrophenol	Learn it
Diazonium salt + phenol in NaOH(aq), below 10 °C → azo dye (–N=N–)	Learn it
OH on a ring is 2,4,6-directing	Learn it
Acidity: carboxylic acid > phenol > water > alcohol	Learn it
Reason: O lone pair (p orbital) overlaps with the ring → O–H weakened, anion stabilised, ring electron density increased	Learn it

How to do it

In the Paper 4 questions we have tagged for this topic (22 questions, 2021–2025; 16 different questions, 6 of them repeated in another variant), the types came up this often. 13 of the 16 different questions mix more than one type, so the counts add up to 36. The phenol part is usually one part of a longer question about arenes, acids or amines.

Question type	Questions
Reactions of phenol: reagents, conditions and products	11
Order and explain relative acidities	8
A phenol group in another molecule	6
Explain why phenol reacts more easily than benzene	5
Esters from alcohols and phenols	5
Make phenol from phenylamine	1

1. Reactions of phenol: reagents, conditions and products (11 questions)

1. **Name the reagent and condition exactly:** "bromine water" or " $\text{Br}_2(\text{aq})$ ", not just "bromine"; "dilute HNO_3 " or " $\text{HNO}_3(\text{aq})$ " at room temperature; " $\text{NaOH}(\text{aq})$ " with the diazonium salt.
2. **Draw the product with the OH still there**, and the new groups at 2, 4 or 6.
3. **Write equations with every product:** 3HBr from bromination, H_2 (or $\frac{1}{2}\text{H}_2$) from sodium, H_2O from NaOH .

Variations you will meet:

- **"Name the two products" with an excess of $\text{Br}_2(\text{aq})$:** 2,4,6-tribromophenol **and** hydrogen bromide.
- **Nitration products with a given M_r (139):** draw 2-nitrophenol and 4-nitrophenol. They must be different; two drawings of the same molecule turned over score nothing.
- **Explain the positions:** the OH group donates electron density to the ring **and** is 2,4-directing. Say both.
- **Identify the reagent for an azo compound** from its structure: split the molecule at $-\text{N}=\text{N}-$. The part that had the OH was the phenol; the other part was the diazonium salt, ArN_2^+ . Name the new group "azo", not "diazo" or "diazonium".
- **Reaction with Na, $\text{NaOH}(\text{aq})$ or $\text{Na}_2\text{CO}_3(\text{aq})$ in a tick table:** phenol reacts with the first two; a carboxylic acid with all three; an alcohol with Na only.
- **Phenoxide as the electrophile's partner.** In $\text{NaOH}(\text{aq})$ phenol becomes $\text{C}_6\text{H}_5\text{O}^-$, whose ring is even more reactive, so it can attack weak electrophiles (even CO_2) at position 2. Draw the mechanism as for benzene: arrow from the ring to the electrophile, the horseshoe intermediate with $+$, then the C–H bond electrons returning to the ring.

2. Order and explain relative acidities (8 questions)

1. **Write the order** in the boxes, most acidic first. Carboxylic acids first, then phenols (a phenol with an electron-withdrawing group such as NO_2 or Cl above plain phenol), then water, then alcohols.
2. **Link acidity to H^+ loss once:** "the more easily the O–H bond breaks / the more stable the anion, the stronger the acid".
3. **Give a structural reason for each compound:**
 - carboxylic acid: the $\text{C}=\text{O}$ group is electron-withdrawing (negative inductive effect); the charge on the carboxylate ion is delocalised over two O atoms;
 - phenol: a lone pair (p orbital) on the O overlaps with / is delocalised into the ring π system;
 - alcohol (including ArCH_2OH): the alkyl or CH_2 group is electron-donating (positive inductive effect), so the O–H is strengthened and the anion destabilised;
 - substituted phenol: an electron-withdrawing group (NO_2 , Cl) makes it more acidic than phenol; an electron-donating one (alkyl) makes it slightly less acidic, but still more acidic than water.

For example, butanoic acid > 3-bromophenol > phenol > water > 2-phenylethanol. When the question compares a phenol with a carboxylic acid, the reason is the carboxylic acid's $\text{C}=\text{O}$ group, not the phenol's lone pair.

3. A phenol group in another molecule (6 questions)

1. **Find every functional group** and name it: phenol (OH on the ring), alcohol (OH on a chain carbon, classify it as primary, secondary or tertiary), carboxylic acid, amide, ester, amine, alkene.
2. **Go through the reagent one group at a time:**
 - $\text{Br}_2(\text{aq})$: Br on each **free** 2, 4 and 6 position of each phenol ring; it also adds across any $\text{C}=\text{C}$; count the HBr formed;
 - $\text{NaOH}(\text{aq})$: the phenol and any COOH lose H^+ (and hot NaOH hydrolyses esters and amides); alcohols are unchanged;
 - Na: every OH (phenol, alcohol, acid) becomes O^-Na^+ , giving $\frac{1}{2}\text{H}_2$ per OH;
 - dilute HNO_3 : one NO_2 at a free 2 or 4 position;
 - an acyl chloride: an ester on each OH (and an amide on any NH_2).
3. **Check the molecular formula** if one is given; it tells you how many atoms were added.

Variations you will meet:

- **Deduce the structure.** An unknown that gives a white precipitate with bromine water, taking up Br atoms, is a phenol (or phenylamine). The number of Br atoms added equals the number of free 2, 4, 6 positions.
- **Naphthols** in a dye synthesis: the coupling partner that is made alkaline is the naphthol.

4. Explain why phenol reacts more easily than benzene (5 questions)

Four points, in this order:

1. A lone pair in a p orbital on the oxygen **overlaps with / is delocalised into** the ring's π system.
2. So the **electron density of the ring increases** (most at positions 2, 4 and 6).
3. So the ring **attracts electrophiles** more and **polarises** Br_2 (or other electrophiles) itself.
4. So no catalyst is needed for bromination, dilute nitric acid replaces the $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture, and the reactions go at room temperature.

When asked for the conditions, give the full set: aqueous bromine, no AlBr_3 needed, room temperature.

"Room temperature" alone is not enough. For a three-way comparison (for example phenol, benzene and benzoic acid), a COOH group withdraws electrons and lowers the ring's electron density, so benzoic acid is harder to nitrate than benzene.

5. Esters from alcohols and phenols (5 questions)

1. **Name the ester:** the alkyl group from the alcohol, then the acid part ending in "-oate". Propan-2-ol gives a "propan-2-yl" (or "1-methylethyl") ester, not a propyl one.
2. **Write the equation** with HCl as the other product.
3. **Draw the mechanism** (nucleophilic addition-elimination), as in "Understand it": lone pair on the alcohol O $\rightarrow \delta^+ \text{C}$; $\text{C}=\text{O}$ electrons $\rightarrow \text{O}$; intermediate with O^- and O^+H ; $\text{C}=\text{O}$ reforms and Cl^- leaves.

Variations you will meet:

- **A phenol with an acyl chloride** gives a phenyl ester. With a molecule holding both OH and NH₂ you can get either an ester or an amide (two isomers).
- **A diol with a di-acyl chloride or a dicarboxylic acid** gives a polyester; with a small ring possible, one molecule of each can give a **cyclic** ester. An ester has no OH, so it does not react with Na.
- **Alcohol + carboxylic acid (AS)**: concentrated H₂SO₄ catalyst, heat, reversible.

6. Make phenol from phenylamine (1 question)

1. Step 1: NaNO₂ and dilute HCl (or HNO₂), **below 10 °C**, giving the diazonium salt.
2. Step 2: warm the solution with water (above 10 °C); N₂ is given off.

Write "NaNO₂", sodium **nitrite**; NaNO₃ is wrong. The same first step starts a dye synthesis, where the cold diazonium salt is added to a phenol in NaOH(aq) instead of being warmed.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Hexanoic acid, CH₃(CH₂)₄COOH, 3-chlorophenol, ClC₆H₄OH, cyclohexanol, C₆H₁₁OH, and water can all act as acids.

(a) Put the four in order of acidity, most acidic first. Explain your order. **[5]**

(b) State which of the three organic compounds react with Na₂CO₃(aq), and write an equation for the reaction of 3-chlorophenol with NaOH(aq). **[2]**

(a) hexanoic acid > 3-chlorophenol > water > cyclohexanol **B1**

The stronger acid loses H⁺ more easily because its O–H bond is weaker, or its anion is more stable. **B1**

- Hexanoic acid: the C=O group withdraws electrons (negative inductive effect), and the carboxylate ion's charge is delocalised over two O atoms. **B1**
- 3-chlorophenol: a lone pair on the O overlaps with the ring's π system, so the charge of the anion spreads over the ring; the electronegative Cl withdraws electrons as well. **B1**

- Cyclohexanol: the alkyl ring donates electrons (positive inductive effect), strengthening the O–H bond and destabilising the anion, so it is less acidic than water. **B1**

(b) Only hexanoic acid reacts with Na_2CO_3 . **B1**



Example 2

A 5.40 g sample of 3-methylphenol is dissolved in 500 cm³ of water, and bromine water is added until no more reacts.

(a) Describe what you would see. **[1]**

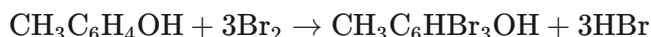
(b) Draw the organic product and name it. Explain why the Br atoms go where they do. **[3]**

(c) Calculate the amount of Br_2 used and the maximum mass of organic product. **[3]**

(d) Explain why benzene needs an AlBr_3 catalyst to react with bromine but 3-methylphenol does not. **[3]**

(a) The orange bromine colour disappears and a white precipitate forms. **B1**

(b) 2,4,6-tribromo-3-methylphenol: the ring carries OH at C1, CH_3 at C3 and Br at C2, C4 and C6. **B1** for the structure, **B1** for the name. The OH group is 2,4,6-directing, and the three positions are all free; the methyl group at C3 also directs to 2, 4 and 6, so the two groups agree. **B1**



(c) $M_r(\text{C}_7\text{H}_8\text{O}) = 7(12.0) + 8(1.0) + 16.0 = 108.0$, so $5.40 \div 108.0 = 0.0500$ mol. **M1**

Br_2 used = $3 \times 0.0500 = 0.150$ mol. **A1**

$M_r(\text{C}_7\text{H}_5\text{Br}_3\text{O}) = 84.0 + 5.0 + 3(79.9) + 16.0 = 344.7$, so the maximum mass is $0.0500 \times 344.7 = 17.2$ g. **A1**

(d) A lone pair (p orbital) on the O overlaps with the ring's π system. **B1** This increases the electron density of the ring. **B1** So the ring polarises the Br_2 molecule and attracts the electrophile itself, without a halogen carrier. **B1**

Example 3

4-chlorophenylamine, $\text{ClC}_6\text{H}_4\text{NH}_2$, can be converted into 4-chlorophenol in two steps.

(a) Give the reagents and conditions for each step. **[3]**

(b) 2.55 g of 4-chlorophenylamine is used. Calculate the volume of gas, measured at room conditions, given off in step 2, and the percentage yield if 1.80 g of 4-chlorophenol is obtained. **[3]**

(c) Instead of step 2, the product of step 1 is added to a cold solution of naphthalen-2-ol in NaOH(aq) . Describe the product, give its molecular formula and name the functional group formed. **[3]**

(a) Step 1: NaNO_2 and dilute HCl **B1**, below 10°C **B1**. Step 2: warm with water. **B1**

(b) $M_r(\text{C}_6\text{H}_6\text{ClN}) = 72.0 + 6.0 + 35.5 + 14.0 = 127.5$, so $2.55 \div 127.5 = 0.0200$ mol. One mole of N_2 forms per mole: $0.0200 \times 24.0 = 0.480 \text{ dm}^3$. **M1 A1**

$M_r(\text{C}_6\text{H}_5\text{ClO}) = 128.5$, so the maximum mass is $0.0200 \times 128.5 = 2.57 \text{ g}$, and the yield is $1.80 \div 2.57 \times 100 = 70.0\%$. **A1**

(c) A coloured (orange-red) azo dye **B1**: the 4-chlorophenyl group joined by $-\text{N}=\text{N}-$ to carbon 1 of naphthalen-2-ol, next to the OH. Molecular formula $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}$ **B1**. The new group is the **azo** group. **B1**

Example 4

Compound **T**, 3-(hydroxymethyl)phenol, $\text{HOC}_6\text{H}_4\text{CH}_2\text{OH}$, has an OH on the ring at C1 and a CH_2OH group at C3.

(a) **T** reacts with an excess of sodium. Write an equation and calculate the volume of hydrogen, at room conditions, from 0.310 g of **T**. **[3]**

(b) Draw the product of **T** with an excess of $\text{NaOH}(\text{aq})$, and explain why only one OH group reacts. **[2]**

(c) **T** reacts with an excess of butanoyl chloride, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$. Draw the organic product and give its molecular formula. **[2]**

(d) Give the molecular formula of the product of **T** with an excess of bromine water. **[1]**

(a) Both OH groups react:



B1. $M_r(\text{C}_7\text{H}_8\text{O}_2) = 124.0$, so $0.310 \div 124.0 = 0.00250$ mol of **T** gives 0.00250 mol of H_2 **M1**, which is $0.00250 \times 24\,000 = 60.0 \text{ cm}^3$. **A1**

(b) $\text{Na}^+ \text{ } ^-\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$: only the ring OH has lost H^+ . **B1** The phenol OH is more acidic than water because the O lone pair is delocalised into the ring; the CH_2OH is an alcohol, less acidic than water, so it does not react with hydroxide ions. **B1**

(c) Each OH becomes a butanoate ester: $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}-\text{C}_6\text{H}_4-\text{CH}_2\text{OOCCH}_2\text{CH}_2\text{CH}_3$, with 2HCl . **B1**
Molecular formula $\text{C}_{15}\text{H}_{20}\text{O}_4$. **B1**

(d) Positions 2, 4 and 6 (relative to the ring OH) are all free, so three Br substitute: $\text{C}_7\text{H}_5\text{Br}_3\text{O}_2$. **B1**

Common mistakes

- **Drawing one Br instead of three.** Bromine water gives 2,4,6-tribromophenol; examiners see the monobromo compound each year. Write "**tribromo**" in the name, and don't forget the 3HBr .
- **Giving only "room temperature" for bromination.** The key condition is that the bromine is **aqueous**, with no catalyst.

- **Stopping the explanation too soon.** Many answers say the lone pair is delocalised into the ring but never say that this **raises the ring's electron density**, or that the ring then **polarises the electrophile**. Each step is a separate mark.
- **Saying OH is electron-donating but not where it directs.** When asked why the products are the 2- and 4-isomers, say the OH is **2,4-directing**.
- **Drawing the same nitrophenol twice.** Two mirror-image drawings of one molecule (or 3-nitrophenol) do not count as the two isomers.
- **Explaining acidity without linking it to losing H^+ .** Say the O–H bond is weakened or the anion is stabilised. "Oxygen is electronegative" is not credited on its own.
- **Using the wrong reason in a comparison.** Phenol is weaker than a carboxylic acid because of the acid's electron-withdrawing C=O group; talking about phenol's lone pair does not explain that.
- **Putting the diazonium charge on the wrong nitrogen.** It is $\text{Ar}-\text{N}^+\equiv\text{N}$, with the + on the nitrogen joined to the ring.
- **Writing NaNO_3 for sodium nitrite, NaNO_2 , and leaving out the alkali for coupling.** Without NaOH(aq) and cold conditions the diazonium salt turns into a phenol instead of a dye.
- **Calling the $-\text{N}=\text{N}-$ group "diazo" or "diazonium".** It is the azo group.
- **Misreading the alcohol.** An ester from propan-2-ol is not the same as one from propan-1-ol. Read the name twice.

How to get the marks

- **Structures:** show every bond that changed, keep the OH on the ring, and put substituents at the right carbons. If you are asked for a "displayed" group, draw all its bonds.
- **Equations:** balanced, with every product (HBr , H_2 , H_2O , HCl , N_2). Use $\frac{1}{2}\text{H}_2$ or double everything for the reaction with sodium.
- **Reagents and conditions:** give both, with concentration and state where they matter: "dilute HNO_3 , room temperature", " $\text{Br}_2(\text{aq})$ ", " $\text{NaNO}_2 + \text{HCl}$, below 10°C ", " NaOH(aq) ".
- **"Explain" relative acidity:** the order earns one mark; then link acidity to O–H strength or anion stability once, and give one structural reason per compound. Mark schemes accept "lone pair" or "p orbital" and "delocalised into" or "overlaps with" the ring.
- **"Explain" easier substitution:** lone pair overlaps with ring $\rightarrow$ more electron density $\rightarrow$ attracts or polarises the electrophile. Three ideas, three marks.
- **Mechanisms:** curly arrows start from a lone pair or a bond and end at an atom or bond; show dipoles and lone pairs when asked, and the charge on the intermediate. Name it in full: "nucleophilic addition–elimination" or "electrophilic substitution".
- **"Suggest"** means apply the rules to an unfamiliar molecule (a naphthol, a drug molecule): the marks go to consistent use of the phenol, alcohol and acid rules, not to recall.
- **Calculations:** use the Data Booklet A_r values and $24.0\text{ dm}^3\text{ mol}^{-1}$, show the moles, and give 3 significant figures unless told otherwise.

Quick check

1. Butan-2-ol and naphthalen-1-ol are shaken separately with NaOH(aq). Which one reacts? Write an equation and explain the difference.
2. 2.44 g of 3,5-dimethylphenol reacts completely with an excess of bromine water. Name the organic product, and find the amount of Br₂ used and the mass of organic product formed.
3. Give the reagents and conditions for the two steps that turn 3-ethylphenylamine into 3-ethylphenol, and say why the first step must be kept cold.
4. 0.600 g of propan-1-ol reacts with an excess of pentanoyl chloride. Name the ester, write the equation, and find the maximum mass of ester.
5. 4-tert-butylphenol, (CH₃)₃CC₆H₄OH, is shaken with dilute nitric acid at room temperature. Why is there only one mononitration product? Give its name and molecular formula.

Answers

1. Naphthalen-1-ol reacts: $\text{C}_{10}\text{H}_7\text{OH} + \text{NaOH} \rightarrow \text{C}_{10}\text{H}_7\text{O}^- \text{Na}^+ + \text{H}_2\text{O}$. Its O lone pair is delocalised into the ring system, which weakens the O–H bond and stabilises the anion, so it is more acidic than water.
Butan-2-ol's alkyl groups donate electrons, so it is less acidic than water and does not react with hydroxide ions.
2. 2,4,6-tribromo-3,5-dimethylphenol (positions 2, 4 and 6 are all free). $M_r(\text{C}_8\text{H}_{10}\text{O}) = 122.0$, so $2.44 \div 122.0 = 0.0200 \text{ mol}$; Br_2 used $= 3 \times 0.0200 = 0.0600 \text{ mol}$. $M_r(\text{C}_8\text{H}_7\text{Br}_3\text{O}) = 358.7$, so the mass is $0.0200 \times 358.7 = 7.17 \text{ g}$.
3. Step 1: NaNO_2 and dilute HCl , below 10°C , giving the diazonium salt. Step 2: warm with water; N_2 is given off. The diazonium salt is unstable and would break down (losing N_2) during step 1 if it warmed up.
4. Propyl pentanoate. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_3\text{COCl} \rightarrow \text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$.
 $0.600 \div 60.0 = 0.0100 \text{ mol}$; $M_r(\text{C}_8\text{H}_{16}\text{O}_2) = 144.0$, so the maximum mass is 1.44 g .
5. The OH directs to positions 2, 4 and 6. Position 4 is taken by the tert-butyl group, and positions 2 and 6 are equivalent, so only one product forms: 4-tert-butyl-2-nitrophenol, $\text{C}_{10}\text{H}_{13}\text{NO}_3$.

Past questions to try

- [9701/42/M/J/23 Q7](#): why phenol brominates easily, then reagents for nitration and azo coupling.
- [9701/43/M/J/22 Q5](#): acidities of an acid, a phenol and an alcohol, and a Na / NaOH / Na_2CO_3 table.
- [9701/42/O/N/21 Q10](#): products of phenol with four reagents, and which reactions ethanol shares.
- [9701/43/M/J/21 Q9](#): deducing a phenol's structure from bromine water, iodoform and ester reactions.