Hydroxy compounds (A Level)

Esters from acyl chlorides, making phenol from phenylamine, the reactions of phenol with bases, sodium, diazonium salts, nitric acid and bromine, and the acidity of water, phenol and ethanol.

32.1 Alcohols

Alcohols react with **acyl chlorides** at room temperature to form **esters** and hydrogen chloride, a faster and irreversible alternative to esterification with a carboxylic acid:

$$CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl$$

(ethanoyl chloride and ethanol give ethyl ethanoate).

Acylation of an alcohol

An alcohol oxygen donates a lone pair to the acyl chloride's carbonyl carbon. After addition and chloride loss, deprotonation gives the ester. The carbonyl group comes from the acyl chloride; the oxygen-linked alkyl fragment comes from the alcohol. This is nucleophilic addition–elimination, not the elimination of water from two OH-containing starting materials.

Worked example: propan-1-ol with ethanoyl chloride gives propyl ethanoate, $CH_3COOCH_2CH_2CH_3$, and HCl. Five carbons are retained in the ester. The reaction is normally much more rapid than acid-catalysed carboxylic-acid esterification and is not the same reversible acid/alcohol equilibrium. Water competes by hydrolysing the acyl chloride, so reagent conditions matter.

> **TRY IT**
>
> Give the ester formed from ethanol and benzoyl chloride.

Answer: Ethyl benzoate, $C_6H_5COOCH_2CH_3$, plus HCl. The phenyl-containing part belongs to the acid-derived fragment.

32.2 Phenol

Phenol, C_6H_5OH, has an –OH group directly on the benzene ring.

Preparation

Phenylamine is treated with HNO_2 (made from $NaNO_2$ and dilute HCl) **below 10 °C** to give a **diazonium salt**; warming the diazonium salt with water then gives phenol (and nitrogen gas):

Note Academy

$$C_6H_5N_2^+Cl^- + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Reactions

Reagent	Product
NaOH(aq)	sodium phenoxide, $C_6H_5O^-Na^+$, and water
Na(s)	sodium phenoxide and H_2
Diazonium salt in NaOH(aq), below 10 °C	an **azo compound** (a coloured dye)
Dilute HNO_3(aq), room temperature	a mixture of **2-nitrophenol** and **4-nitrophenol**
Br_2(aq), room temperature	**2,4,6-tribromophenol** (white precipitate; the bromine water is decolourised)

Phenol is a stronger acid than ethanol and water but a weaker acid than carboxylic acids, so it reacts with NaOH, but **not with sodium carbonate** (no CO_2).

Why phenol is much more reactive than benzene

The lone pair on the oxygen overlaps with the delocalised π system, **increasing the electron density of the ring**. The ring is attacked more readily by electrophiles, so nitration needs only **dilute** nitric acid at room temperature (benzene needs concentrated acids at 25–60 °C), and bromination needs no catalyst, with $Br_2(aq)$ replacing three hydrogens (benzene needs a carrier catalyst and gives mono-substitution). The –OH group **directs to the 2-, 4- and 6-positions**.

Acidity of water, phenol and ethanol

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Phenol is a **weak acid** ($pK_a \approx 10$), appreciably stronger than water and ethanol. Do not confuse water's $pK_w \approx 14$ at 298 K with an ordinary molecular-acid pK_a; these refer to different equilibrium conventions.

- In the **phenoxide ion** the negative charge on oxygen is **delocalised** into the ring through the overlap of an oxygen p orbital with the π system, so the ion is **stabilised** and the equilibrium lies further to the right.
- In the **ethoxide ion** the alkyl group is **electron-donating**, which **intensifies** the negative charge on oxygen, so the ion is less stable.
- Water has no donating group.

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Order of acid strength: **phenol > water > ethanol**. (With carboxylic acids: carboxylic acid > phenol > water > alcohol.)

Other phenolic compounds, such as naphthol, react in the same way.

Worked transfer — naphthol: identify the OH directly attached to the fused aromatic system. It can lose its proton to NaOH to form a naphthoxide salt, and the electron-rich aromatic system can undergo electrophilic substitution or azo coupling. Do not copy phenol's precise three-bromine product onto every naphthol drawing: available positions and the fused-ring structure differ. Apply the same acid–base and activation principles, then use any stated product-position information.

> **Test for phenol: it gives a white precipitate with bromine water, and a violet colour with neutral aqueous iron(III) chloride. Alcohols give neither.**

Phenol and a phenyl-containing alcohol are different

In phenol, oxygen is directly attached to an aromatic carbon, permitting its lone pair to overlap with the ring. In phenylmethanol, $C_6H_5CH_2OH$, the intervening CH_2 interrupts that direct overlap and the OH behaves as an ordinary primary alcohol. Do not infer phenol reactions from a benzene ring anywhere in the molecule.

Worked comparison: phenol reacts with aqueous NaOH to form phenoxide because its conjugate base is sufficiently stabilised. Phenylmethanol is not usefully converted to its alkoxide by aqueous NaOH under the same conditions. Phenylmethanol can undergo ordinary primary-alcohol oxidation to an aldehyde and then acid; phenol does not simply form that same side-chain oxidation sequence because it has no CH_2OH carbon.

> **TRY IT**
>
> Which has a phenolic OH: C_6H_5OH or $C_6H_5CH_2OH$? Explain the structural reason.

Answer: C_6H_5OH only. Its oxygen directly bonds to a ring carbon; the other compound has OH on a separate aliphatic carbon.

Acidity: stabilise the conjugate base

Compare the products after proton loss. Phenoxide spreads negative charge through overlap with the aromatic system, whereas ethoxide has more localised negative charge and electron donation from alkyl. This makes phenol more willing to donate a proton than ethanol in the syllabus comparison. A carboxylate is still more strongly stabilised by charge delocalisation over two oxygens, so carboxylic acids are generally stronger.

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Reaction with NaOH is acid–base chemistry and makes water. Reaction with sodium metal is redox and makes hydrogen. Neither reaction removes the whole oxygen atom from the ring. To distinguish phenol from a carboxylic acid, hydrogencarbonate effervescence is useful: a carboxylic acid liberates CO_2, while phenol does not give that characteristic gas test. Avoid treating the absence of gas as proof of no acid–base interaction of any kind with every carbonate system.

Worked calculation: 0.0100 mol phenol consumes 0.0100 mol NaOH in phenoxide formation. With sodium metal, the same phenol amount releases 0.00500 mol H_2. The difference follows the balanced equations, not two different acidities of the sample.

Why electrophilic substitution is easier

Oxygen lone-pair donation increases electron density in the aromatic system, particularly at positions favoured for 2/4/6 substitution. Bromine water can therefore react without a separate halogen carrier. With an excess under the usual conditions, three ring hydrogens are replaced to form 2,4,6-tribromophenol. Both decolourisation and the white precipitate are important observations.

Worked equation: $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$. The OH group stays attached and three H atoms on the ring are replaced. Addition of six bromine atoms across hypothetical isolated double bonds is not the correct phenol product.

> **TRY IT**
>
> Why is bromine-water decolourisation alone insufficient to distinguish phenol from an alkene?

Answer: Both can consume bromine. Phenol's characteristic precipitate and other evidence distinguish the aromatic substitution from alkene addition. Identify the product and observations, not just loss of colour.

Diazotisation, hydrolysis and coupling

Cold nitrite/acid converts phenylamine to a diazonium salt. Keep this stage below the stated low-temperature limit to avoid premature decomposition. Warming with water then replaces the diazonium group by OH and releases nitrogen. Cooling and warming therefore belong to different stages and have deliberately different purposes.

Coupling a cold diazonium solution with alkaline phenol instead forms an azo linkage, usually at the available position para to OH. Phenoxide is an electron-rich coupling partner. The extended conjugated structure can absorb visible light, explaining strongly coloured products. An azo linkage is N=N, not a nitrile C≡N or an amide C–N bond.

Note Academy

> **TRY IT**
>
> What happens if the diazonium solution is deliberately warmed with water rather than coupled with phenoxide?

Answer: It can hydrolyse to phenol with nitrogen evolution, rather than form the intended azo compound. The next reagent and temperature determine which transformation occurs.

Chapter check: distinguish direct phenolic attachment, explain acidity through the conjugate base, retain the ring during substitution and separate cold diazotisation from the later warming or coupling step.

References and further reading

Scope follows section 32 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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