

CAIE Chemistry A-level

32: Hydroxy Compounds (A-level only)

Notes

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Alcohols

Formation of Esters by Acylation with Acyl Chlorides

Esters can also be produced from **alcohols** and **acyl chlorides**. Alcohol reacts vigorously with acyl chlorides, releasing steamy fumes of hydrochloric acid.



O-H

Phenol

Phenol is an aromatic hydrocarbon consisting of one alcohol group bonded to the benzene ring:

Phenyl benzoate:

Benzoyl chloride is very **unreactive** because the -COCI group is directly attached to a **stable benzene ring**. To produce the ester phenyl benzoate, phenol is first converted into an ionic compound by **dissolving it in sodium hydroxide**. This produces the **phenoxide** ion:



The **phenoxide ion** is **more reactive** than the phenol so this ion can react with benzoyl chloride to produce phenyl benzoate:





Reactions with Bases

Phenol is a **weak acid**. A hydrogen ion can be removed from the hydroxyl group and transferred to a base. The position of **equilibrium** for the reaction below lies far to the left which means that phenol is a weak acid.



Phenol is able to donate a hydrogen ion because the **phenoxide ion** is **relatively stable**. The **lone pair** on the oxygen atom is delocalised into the **pi system** which is above and below the benzene ring. This means that the **negative charge is dispersed** among the carbon atoms so the compound is more stable.

Reaction with sodium hydroxide

When phenol reacts with sodium hydroxide, colourless sodium phenoxide is formed.



Reaction with sodium carbonate

Phenol isn't acidic enough to react with sodium carbonate.

Reactions with Sodium

Phenol reacts with metals in the same way that most acids. **Hydrogen gas** and a salt are produced. The reaction occurs **slower** than comparable acid-metal reactions because phenol is a **weak acid**.







Reactions with diazonium salts

Diazonium salts contain the diazonium ion, $\mathbf{R}-\mathbf{N}_{2}^{+}$ (where R is any organic group). In the case of the following example, we will be looking at the diazonium ion when it is attached to a **benzene** ring.

 \bigvee N⁺ N

Before a diazonium salt is reacted with phenol, phenol is dissolved in **sodium hydroxide** to give the **phenoxide ion**:



Cold **benzenediazonium chloride** is then added to the **sodium phenoxide** solution. The diazonium and phenoxide ions react together to form an **azo compound**. An azo compound contains two benzene rings that are joined together with a nitrogen bridge. The product can be identified as a **yellow solution** or **precipitate**.



Nitration and Bromination of the Aromatic Ring

Phenol is **more reactive than benzene** because it contains an -OH functional group. The lone pair on the oxygen atom is delocalised into the **pi system**. This **increases the electron density**, making phenol more likely to be **attacked by electrophiles**.

The effect of the OH group is sometimes referred to as the **2,4-directing effect**. This is because the incoming groups tend to bond to the second and fourth carbons from the hydroxyl group.

Nitration

Phenol reacts with dilute and concentrated nitric acid:

• Dilute nitric acid

The 2,4-directing effect of the hydroxyl group causes a mixture of **2-nitrophenol** and **4-nitrophenol** to be produced. The reaction for 2-nitrophenol is shown below.

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Concentrated nitric acid
The compound 2,4,6-trinitrophenol is formed.



Bromination

When bromine water is added to a solution of phenol, the orange bromine water is decolourised. **2,4,6-tribromophenol (white precipitate)** and hydrogen bromide are formed.



Relative Acidities of Water, Phenol and Ethanol

The relative acidities are as follows: phenol > water > ethanol

- Phenol is the most acidic because the phenoxide ion (formed when phenol donates a proton) is relatively stable. The lone pair on the oxygen atom is delocalised into the pi system meaning the negative charge is dispersed among the carbon atoms. This means that phenol is more likely to donate a hydrogen ion than water or ethanol.
- Ethanol and water have similar acidities but ethanol is the least acidic. This is because of the positive inductive effect. The alkyl group in the ethoxide ion "pushes" electrons away from itself, towards the oxygen. This increases the electron density of the oxygen, making it more likely to bond to a hydrogen ion and reform ethanol.

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