



CIE A Level Chemistry



Your notes

32.2 Phenol

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- * Acidity of Phenols
- * Nitration & Bromination of Phenol
- * Reactions of Other Phenolic Compounds



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Producing Phenol

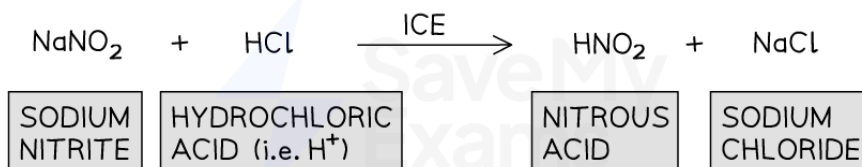
Production of Phenol

- Phenols are organic compounds characterised by the presence of an -OH group which is attached to a benzene ring
- Phenols can be produced by the reaction of **phenylamine** with **nitrous acid** (HNO_2)

Production of phenol

- Phenols can be prepared from phenylamines under the following reaction conditions:
 - NaNO_2 with dilute acid (to form HNO_2)
 - Ice to keep the temperature below 10°C (step 1)
 - Heat (step 3)
- This reaction involves three steps:
 - Step 1** - The HNO_2 is so unstable that it needs to be prepared in a test-tube by reacting sodium nitrite (NaNO_2) and dilute hydrochloric acid (HCl) while keeping the temperature below 10°C using ice

Forming nitrous acid, HNO_2

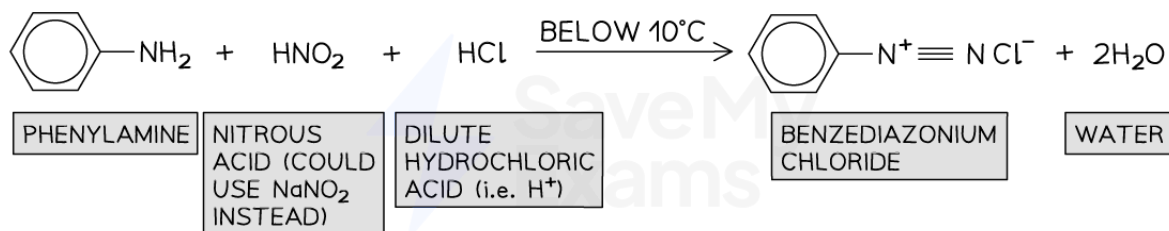


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Nitrous acid can be prepared in a test-tube by reacting sodium nitrate with dilute hydrochloric acid

- Step 2** - Phenyl amine is then reacted with the HNO_2 to form an **unstable diazonium salt**

Forming benzenediazonium chloride

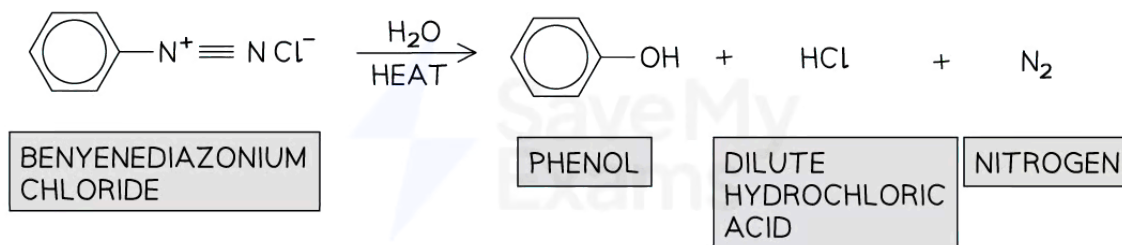


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Benzenediazonium chloride is an unstable diazonium salt

- **Step 3** – The diazonium salt is so unstable that it will **thermally decompose** when **heated** to form a **phenol**

Forming phenol



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Phenol is formed by the thermal decomposition of the unstable diazonium salt, benzenediazonium chloride



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Reactions of Phenol

Reactions of Phenol

- Phenols can undergo many types of reactions as both the **electron-rich benzene ring** and the **polar -OH group** can participate in chemical reactions
- Some of the reactions of phenols include:
 - With bases
 - With reactive metals
 - With diazonium salts
 - Nitration
 - Bromination

Reactions of the -OH group in phenols

- The -OH group in phenols has a **slightly acidic character**
- It can therefore act as an **acid** and take part in **acid-base reactions**

Reaction with bases

- Phenols are **only slightly soluble** in water due to the large non-polar benzene ring
- However, they do dissolve in alkaline solutions and undergo **acid-base** reactions with **bases** to form a **soluble salt** and **water**

Phenol in acid-base reactions



Phenols are weak acids and undergo acid-base reactions in alkaline solutions

Reaction with reactive metals

- Molten phenols** react **vigorously** with reactive metals such as **sodium (Na)**
- This is also an **acid-base** reaction
- Now, a soluble salt is formed and **hydrogen gas** is given off

Phenol with metals reaction



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Molten phenols react vigorously with reactive metals to form a soluble salt and hydrogen gas

Reaction with diazonium ions

- **Diazonium ions** are very reactive compounds containing an $-\text{N}_2^+$ group
- When phenols are **dissolved** in sodium hydroxide (NaOH), a solution of **sodium phenoxide** is obtained
- This solution is cooled in **ice** and **cold diazonium ion** is added to the sodium phenoxide
- After the reaction has occurred, a **yellow-orange** solution or precipitate of an **azo compound** is formed
- These are compounds in which **two benzene** rings are linked by a **nitrogen bridge**

Phenol in diazonium ion reactions

STEP 1



STEP 2



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Azo compounds are formed from the reaction of phenols with diazonium ions

Reactions of the aromatic ring in phenols

- Phenols react more **readily** with **electrophiles** compared to benzene
- This is because one of the lone pairs of electrons on the oxygen atom in $-\text{OH}$ overlaps with the π bonding system



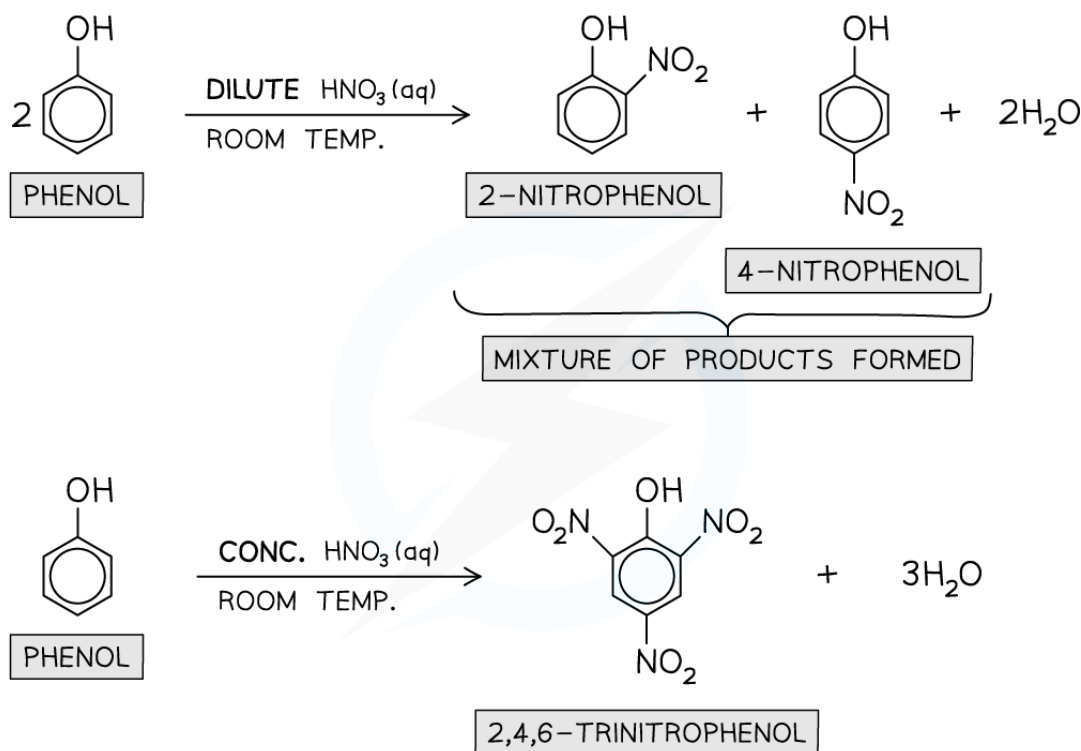
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- This increases the **electron density** of the benzene ring making it more **susceptible** to **electrophilic attack**
- The -OH group in phenols is **activating** and **directs** incoming electrophiles to the **2, 4, and 6 positions**

Nitration

- Phenols can undergo **electrophilic substitution** reactions when reacted with **dilute nitric acid** (HNO_3) at **room temperature** to give a mixture of **2-nitrophenol** and **4-nitrophenol**
 - When **concentrated** HNO_3 is used, the product will be 2,4,6-trinitrophenol instead
- A hydrogen atom in the benzene ring is **substituted** by a nitro ($-\text{NO}_2$) group
- This is also known as the **nitration** of phenol

Phenol in nitration reactions



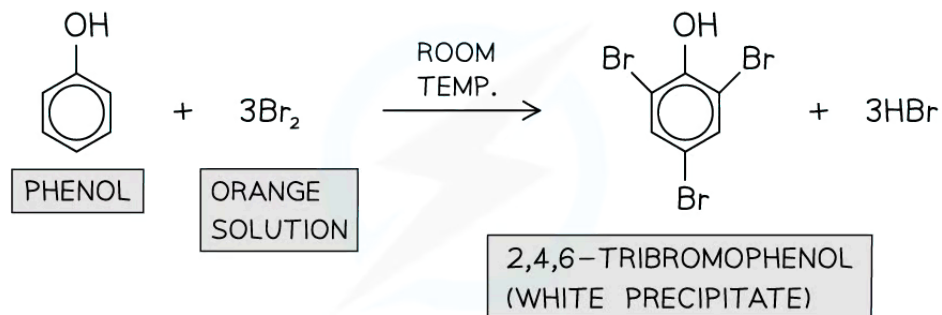
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Phenols undergo nitration when reacted with dilute HNO_3 at room temperature

Bromination

- Phenols also undergo **electrophilic substitution** reactions when reacted with **bromine water** at **room temperature**
- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol
- This is also known as the **bromination** of phenol

Phenol in bromination reactions



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Phenols undergo bromination when reacted with bromine water at room temperature



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Acidity of Phenols

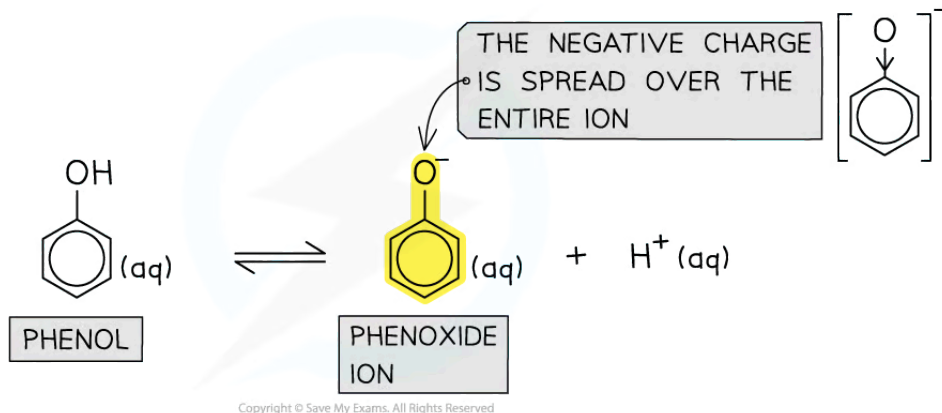
Acidity of Phenols

- Although phenol compounds contain an **alcohol** (-OH) group, they are **weakly acidic**
- This is due to the **delocalisation** of one of the lone pairs from the oxygen atom into the aromatic ring
- This increases the electron density of the ring and increases the acidic behaviour

Delocalisation of charge density

- The **conjugate base** of phenol is the **phenoxide ion**
- In the phenoxide ion, the **negative charge** on the oxygen is spread out over the entire ion
- This is possible as **one of the lone pairs** on the oxygen atom **overlaps** with the delocalised π system of the ring
- Because of this delocalisation, there is less **charge density** on the oxygen atom
- The H^+ ions are therefore not strongly **attracted** to the phenoxide ion and are less likely to **reform** the **phenol** molecule
- This means that phenol is more likely to **lose** a proton (and act as an **acid**) rather than to **gain** a proton (and act as a **base**)

The equilibrium between phenol and the phenoxide ion



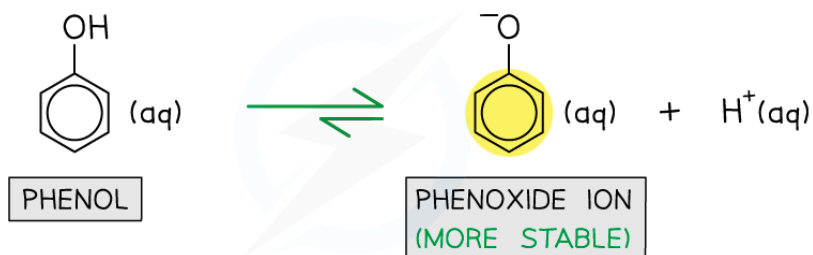
The negative charge is spread over the ion, causing the electrons to become less available for bonding with an incoming proton

Stability of the conjugate base

- Phenol **ionises** to form a **more stable** negative **phenoxide** ion with its negative charge **spread out**
- This means that phenol is **more likely** to undergo **ionisation**
- The equilibrium position, therefore, lies further to the **right** and a higher proportion of phenol molecules **donate a proton** compared to for example water and ethanol
- The phenol compound is, therefore, more likely to act as an **acid** rather than a base

- Therefore, the position of equilibrium lies:
 - Further to the **right-hand side** favouring the **dissociated phenoxide ions**
 - Further to the **left-hand side** favouring the **undissociated ethoxide and hydroxide ions**

The equilibrium position of phenol and the phenoxide ion



Since the phenoxide ion formed from the ionisation of phenol is more stable than phenol itself, the equilibrium position lies further to the right-hand-side and phenol is more likely to act as an acid rather than a base



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Relative Acidities of Water, Phenol & Ethanol

- The pK_a is a measure of the acidity of a substance
- The values of water, phenol, and ethanol show that phenol is a **stronger** acid than ethanol and water

Relative acidity of ethanol, water & phenol table

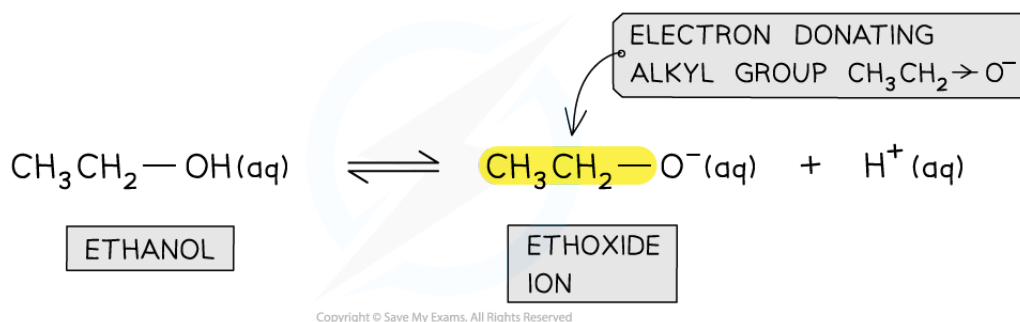
Acid	Dissociation	pK_a at 25 °C
Ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16
Water	$H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$	14
Phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10

- The order of acidity can be explained by looking at their **conjugate bases** which are formed from the dissociation of the compounds

Delocalisation of charge density

- In the **phenoxide ion** (which is the conjugate base of phenol) the charge density on the oxygen atom is **spread out** over the entire ion
- As a result, the electrons on the oxygen atom are **less available** for bond formation with a proton (H^+ ion)
- The **conjugate base** of ethanol is the **ethoxide ion**
- The **ethyl** group in the ion is an **electron-donating** group that donates electron density to the oxygen atom
- As a result, the electron density on the oxygen atom is **more readily available** for bond formation with a H^+ ion

The equilibrium between ethanol and the ethanoate ion





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The electron-donating alkyl group in the ethoxide ion concentrates charge density on the oxygen atom which can more easily bond an H^+ ion

- The **conjugate base** of water is the **hydroxide ion**
- Since the charge density of the oxygen atom cannot become delocalised over a ring, the hydroxide ion more readily accepts an H^+ ion compared to the phenoxide ion
 - Water is, therefore, a **stronger base** compared to phenol
- However, as there are no **electron-donating** alkyl groups, less negative charge is concentrated on the oxygen atom which therefore less readily accepts an H^+ ion compared to the ethoxide ion
 - Water is, therefore, a **weaker base** compared to ethanol

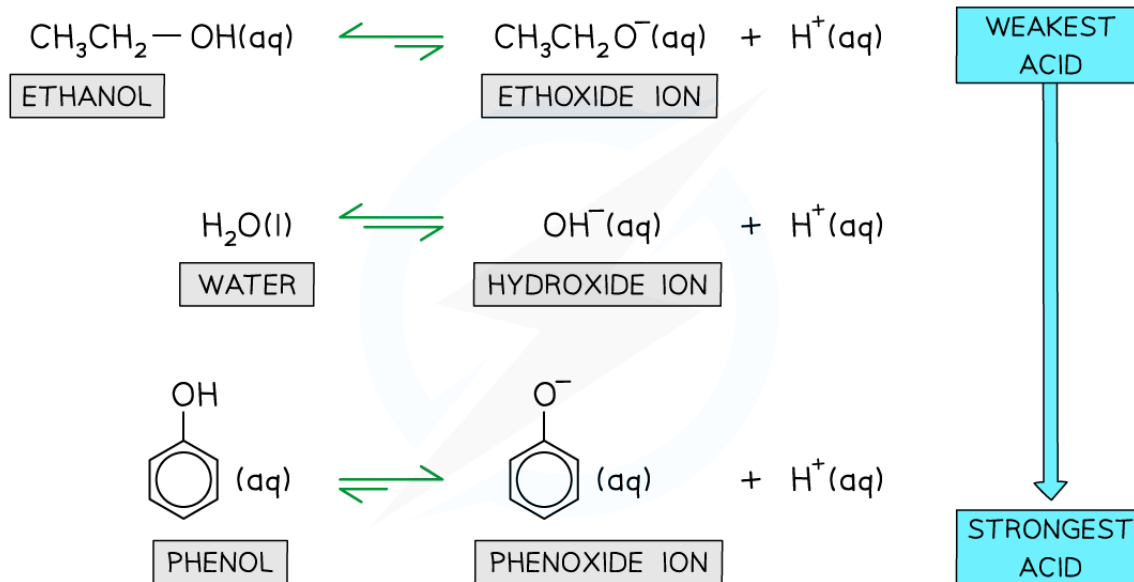
The equilibrium between water and the hydroxide ion



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The hydroxide ion lacks an aromatic ring and electron-donating alkyl groups so water is a stronger base than phenol but a weaker base than ethanol

- Therefore, the position of equilibrium lies:
 - Further to the **right-hand side** favouring the **dissociated phenoxide ions**
 - Further to the **left-hand side** favouring the **undissociated ethoxide and hydroxide ions**
- Relative equilibrium positions for the dissociation of ethanol, water and phenol**



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The relative equilibria for the dissociation of ethanol, water and phenol mean that ethanol is the weakest acid, while phenol is the strongest acid



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Nitration & Bromination of Phenol

Nitration & Bromination of Phenol

- Compared to **benzene**, **phenol** reacts **more readily** with **electrophiles**
- This is because **one of the lone pairs** of electrons on the oxygen atom in phenol **overlaps** with the π bonding system of the benzene ring
- As a result, there is now an **increased electron density** in the ring
- The **electron-donating** -OH group in phenol, therefore, **activates** the benzene ring and **directs** incoming **electrophiles** to the 2, 4, and 6 positions
- The increased reactivity of phenol means that different reagents and conditions are used for **electrophilic substitution** reactions of phenols compared to benzene

Nitration

- Nitration is an example of an **electrophilic substitution** reaction
- The nitration of **benzene** requires a mixture of **concentrated** nitric acid (HNO_3) and sulfuric acid (H_2SO_4) **refluxed** with benzene between **25 °C and 60 °C**
- Since phenol is more reactive, nitration can occur under **milder conditions** by reacting it with **dilute** nitric acid at **room temperature**
 - If **concentrated** nitric acid is used, 2,4,6-trinitrophenol is formed

Bromination

- Bromination is another example of an **electrophilic substitution** reaction
- Benzene will undergo bromination **only** when reacted with **pure bromine** (not a solution) **and** in the presence of an anhydrous aluminium bromide (AlBr_3) **catalyst** at **room temperature**
- Phenol on the other hand readily reacts with **bromine water** in the **absence** of a catalyst

Reagents & conditions for nitration and bromination of phenol & benzene table

Reaction	Benzene	Phenol
Nitration	Concentrated nitric acid and concentrated sulfuric acid Reflux between 25 °C and 60 °C	Dilute nitric acid Room temperature
Bromination	Pure bromine Aluminium bromide (AlBr_3) catalyst	Bromine water Room temperature

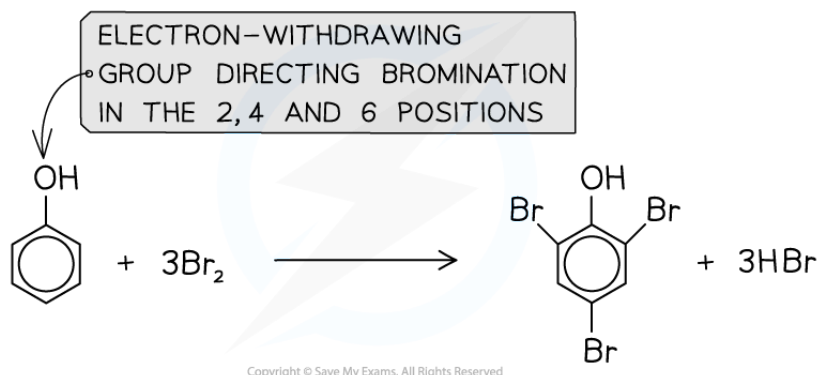


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Directing Effects of Hydroxyl Group on Phenol

- Phenols consist of a hydroxyl (-OH) group attached to a benzene ring
- The **oxygen** atom in this hydroxyl group **donates** electron density into the ring
- One of the lone pairs of the oxygen atom **overlaps** with the π system of the benzene ring and becomes **delocalised** causing an **increased** electron density in the aromatic ring
- Due to the increased electron density, the benzene ring is now more likely to undergo **electrophilic attack** and becomes **activated**
- The hydroxyl group of the phenol directs the incoming electrophiles to the 2, 4, and 6 positions
- An example is the bromination of phenol
 - The bromine acts as an electrophile and **substitutes** a hydrogen atom in the benzene ring
 - The substitution of the hydrogen atom can occur on the 2, 4, or 6 positions

Bromination of phenol



The hydroxyl group in phenol directs bromination in the 2, 4 and 6 positions



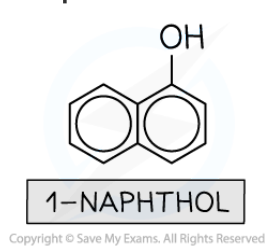
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Reactions of Other Phenolic Compounds

Reactions of Other Phenolic Compounds

- Phenolic compounds are those that contain a **phenol** functional group
 - An example of a phenolic compound is **1-naphthol**

1-naphthol molecule



1-Naphthol is a phenolic compound

- 1-Naphthol contains a phenol group attached to another benzene ring
- Just like with phenol, the -OH group in 1-naphthol is also **electron-donating** and **activates** the benzene ring to **electrophilic substitution** reactions
- The **electrophiles** are directed to the 2 and/or 4 positions
- Substitution at the 6 position is not possible as there is no hydrogen atom on this carbon
 - This carbon is bonded to a carbon atom of the second benzene ring
- 1-Naphthol and other phenolic compounds react in a similar way as phenol