

Phenols

Phenols contain one or more -OH groups directly bonded to the benzene ring.

Physical Properties

- **Hydroscopic**
- **Solid at rtp**
→ Strong hb between phenol molecules
- **Slightly soluble in cold water (emulsion formed), bigger molecules containing phenol FG tend to be insoluble.**
→ Large non-polar BR
- **Solubility increase with temperature**
→ Energy supplied to overcome id-id i between BR

Reactivity

Resonance effect: Lone pair of electrons in p orbital of O atom is delocalised into the π electron cloud of BR through sideways overlap of p orbital of O and the π electron cloud of BR

Implications:

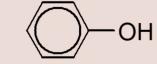
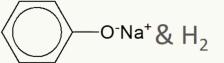
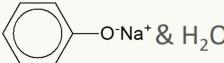
1. C-O bond has partial double bond character → harder to break
→ **don't undergo nsub rxns**
2. Lone pair of e^- on O atom less available to attack an electrophilic centre → **phenol is a weaker nphile than alcohols**
→ convert to alkoxide (stronger nphile with full negative charge) for nsub rxns
3. e^- density of BR increases → **phenol undergo esub more readily than benzene**

Acidity



More stable the alkoxide anion, stronger the acid (POE left)

Acid strength: ethanol < water < phenol < carboxylic acids

	CH ₃ CH ₂ OH		CH ₃ COOH
Na	CH ₃ CH ₂ O ⁻ Na ⁺ & H ₂		CH ₃ COO ⁻ Na ⁺ & H ₂
NaOH	No reaction		CH ₃ COO ⁻ Na ⁺ & H ₂ O
Na ₂ CO ₃	No reaction	No reaction	CH ₃ COO ⁻ Na ⁺ & CO ₂ & H ₂ O

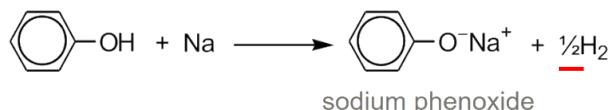
★ Important to distinguish between EDG/ EWG explanation (Arenes) and EDS/ EWS explanation (Hydroxyl Cmpds)

EDS (e.g. -CH ₃ , -OH, -NH ₂)	EWS
Reduce delocalisation of negative charge on O atom into BR → destabilising the anion → decrease acid strength	Increase delocalisation of negative charge on O atom into BR → stabilising the anion → increase acid strength

Reactions

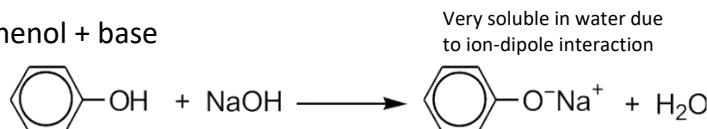
1. 3° alcohols and phenols are resistant to oxidation

2. Phenol + reactive metal



Observation: Colourless, odourless H_2 gas evolved extinguishes lighted splint with a 'pop' sound

3. Phenol + base



Observation: Phenol dissolves in NaOH (aq) to give a colourless solution

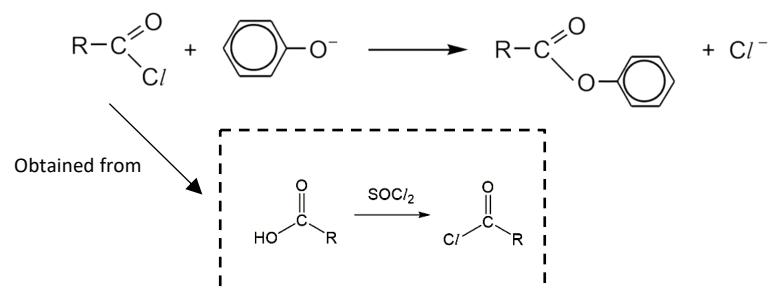
4. Formation of ester

Before ester can be formed, need to make carboxylic acid a stronger electrophile (RCOCl) and phenol, a stronger nucleophile (alkoxide).

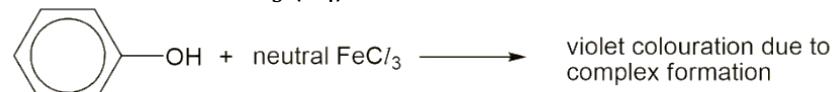
Step 1: Acid-base reaction



Step 2: Nucleophilic (acyl) substitution



5. Phenol + neutral FeCl_3 (aq)

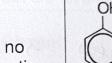
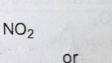
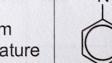
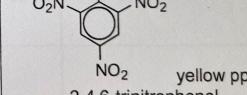


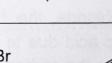
Identification Test for Phenols

6. Electrophilic Substitution

To control esub and avoid polysubstituted pdts as phenol undergo esub readily, use rtp/dilute conditions.

N.B. -OH is a stronger 2-4 director compared to -CH₃ group

Reagent	Reaction Conditions		Products of Substitution	
	benzene	phenol	benzene	phenol
dilute HNO_3	-	room temperature	no reaction	 or  2-nitrophenol 4-nitrophenol
conc HNO_3	conc H_2SO_4 , maintained at 55 °C	room temperature		 yellow ppt 2,4,6-trinitrophenol

Reagent	Reaction Conditions		Products of Substitution	
	benzene	phenol	benzene	phenol
Br_2	aqueous Br_2 , room temperature		 2,4,6-tribromophenol	 white ppt
	Fe or FeBr_3 or anhydrous Al/Br_3 catalyst	Br_2 in CCl_4	 2-bromophenol	 4-bromophenol

Br_2 is non polar

CCl_4 non polar $\rightarrow \text{Br}_2$ well solvated \rightarrow less reactive

H_2O polar \rightarrow no favourable interaction with Br_2 \rightarrow more reactive