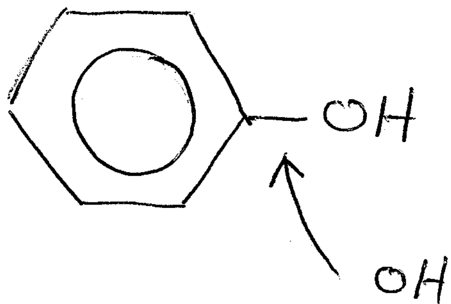
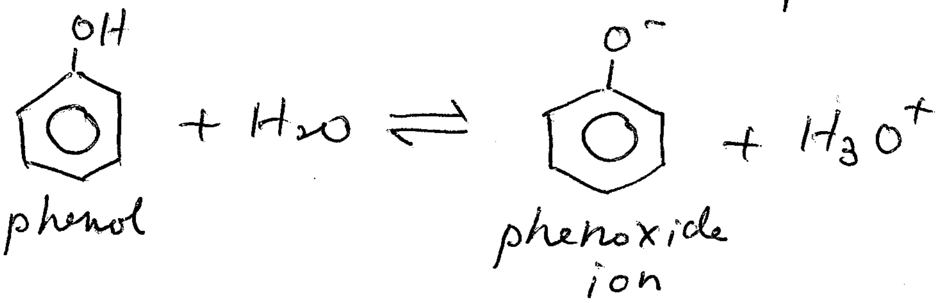
Phenol



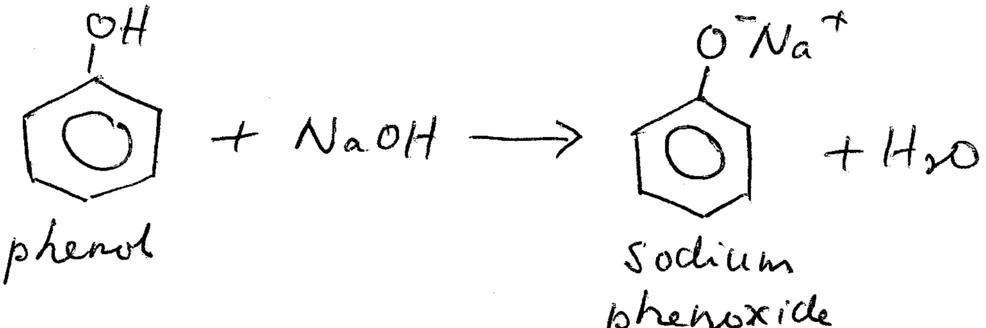
OH group attached directly to a benzene ring

Acidity of Phenol

1. Phenol + H_2O – weak acid (pH ~ 5 to 6)



2. Phenol + $NaOH_{(aq)}$ → salt (ionic)



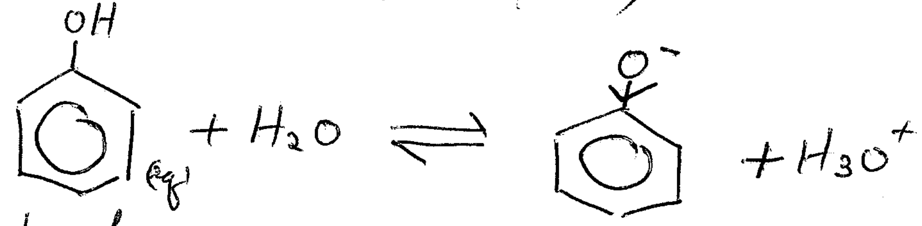
(alcohol dont react with NaOH)

3. Phenol + carbonate $\nrightarrow$

phenol – weaker acid than ~~carbonic~~ carboxylic acid.

Relative acidities of phenol, water and ethanol

order of acid strength: phenol > water > ethanol
pKa (25°C): 10.0 14.0 16.0



phenol

phenoxide ion (conjugate base) with negative charge spread over the whole ring

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

$(H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)})$

hydroxide ion (conjugate base)

$C_2H_5OH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2 \rightarrow O^-_{(aq)} + H_3O^+_{(aq)}$

ethoxide ion (conjugate base) with negative charge concentrated on the oxygen.

Charge distribution explaination

$C_6H_5O^-(aq)$ has its negative charge spread over the whole ion as one of the lone pairs on the oxygen atom overlaps with the delocalised π bonding system in the benzene ring.

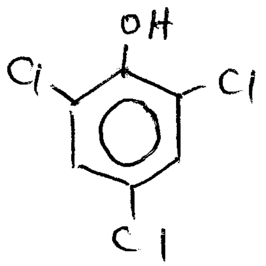
This delocalisation reduces the charge density of negative charge on the phenoxide ion compared with $OH^-(aq)$ or $C_2H_5O^-(aq)$.

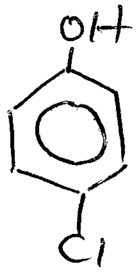
Therefore $H^+(aq)$ ions are not as strongly attracted to the phenoxide ion as they are to $OH^-(aq)$ or $C_2H_5O^-(aq)$ ions, making phenoxide ions less likely to re-form the undissociated molecules.

(Equilibrium appwach:
phenol ionises to form a more stable negative ion, so the ionisation of phenol is more likely. This results in the position of equilibrium lying to the right-hand side (i.e. more molecules donating H^+ ion) than the other equations.)

Ethanol is a weaker acid than water due to the electron-donating alkyl (ethyl) group attached to the oxygen atom in the ethoxide ion. This has the effect of concentrating more negative charge on the oxygen atom, which more readily accepts an H^+ ion. Hence, the position of equilibrium lies further to the left-hand side, favouring the undissociated ethanol molecules.

Effect of Electron-withdrawing groups in benzene ring on the acid strength of phenol



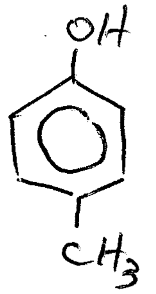


2,4,6-trichlorophenol 4-chlorophenol phenol

pKa 7.6 9.4 10.0

Acidity > >

Electron-donating groups in the benzene ring decreases the acid strength of phenol

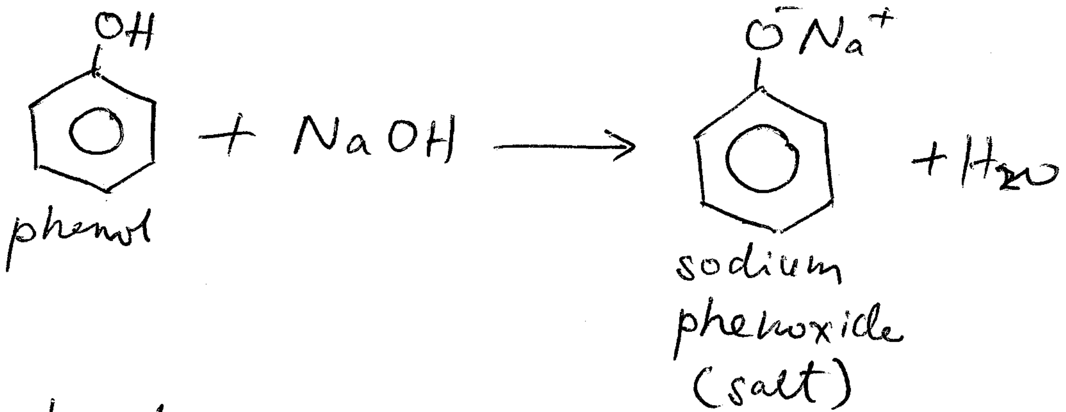


acidity <

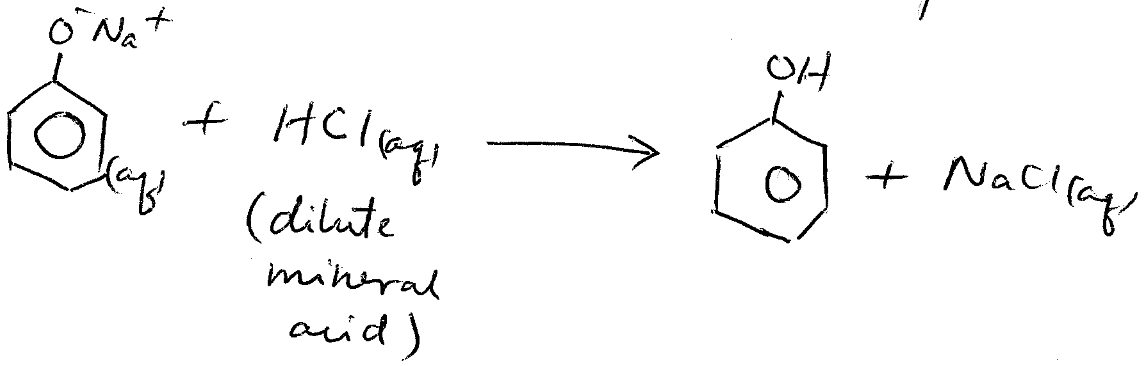
Reactions of Phenol

1. Reaction with Bases
2. Reaction with Sodium
3. Nitration
4. Halogenation.

1. Reaction with Bases



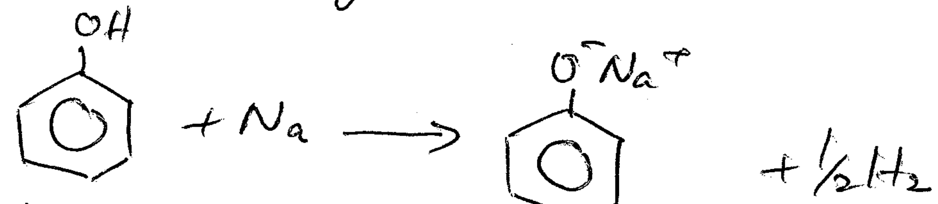
phenol is recovered from sodium phenoxide.



2. Reaction with Sodium

Reagent : sodium

Observation : gas evolved (H_2), rxn more vigorous than with ethanol



phenol

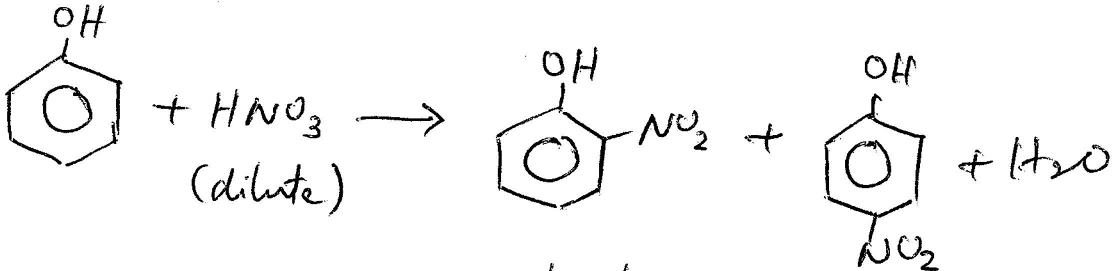
sodium phenoxide

3. Nitration

(1) Reagent : Dilute HNO_3 (phenol readily nitrated, H_2SO_4 not required)

Condition : Room temperature

Product : 2-nitrophenol and 4-nitrophenol (mixture)

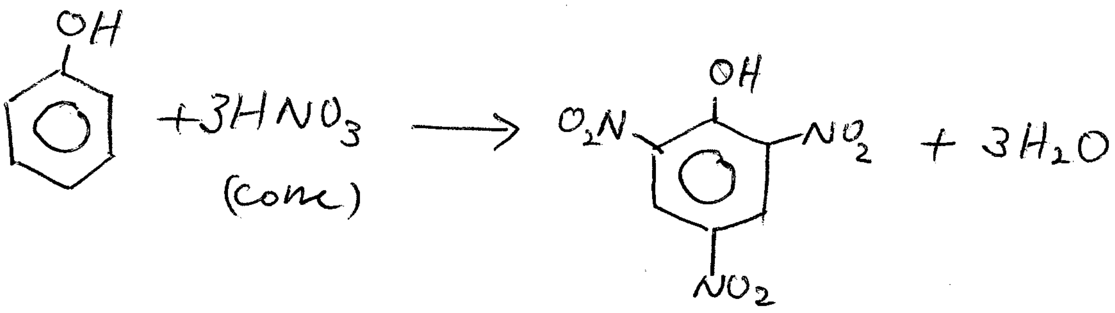


2-nitrophenol 4-nitrophenol

unshared pair of electrons on the O atom is delocalised into the benzene ring → making it more susceptible to electrophilic attack.

The –OH group activates the ring towards electrophilic substitution (substitution at 2- or 4- position)

(ii) Reagent : Conc. HNO_3
Condition : Room Temperature
Product : 2,4,6-trinitrophenol



2,4,6-trinitrophenol
(picric acid)

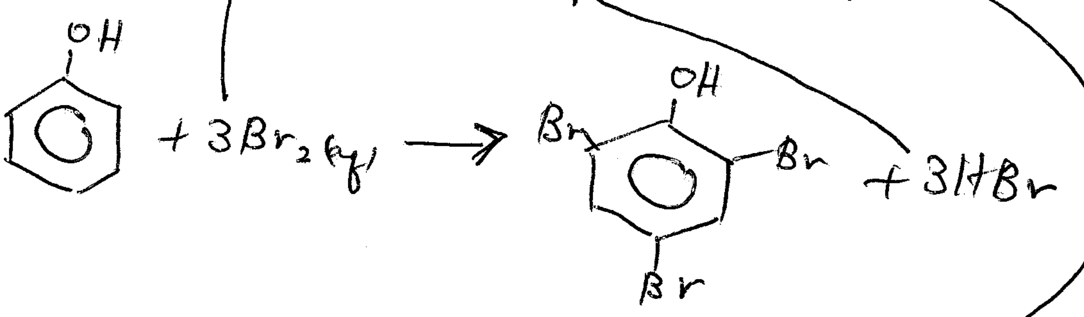
4. <u>Halogenation</u>

more readily v.s benzene, simple conditions required:
- no halogen-carrier needed
- aqueous halogen solution can be used.

and : more than one halogen enter the ring.

because -OH group is electron donating → activates the ring.

Reagent : Bromine water
Condition : room temperature
Observation : reddish brown solution decolourised + steamy fumes, white ppt.



2,4,6-tribromophenol