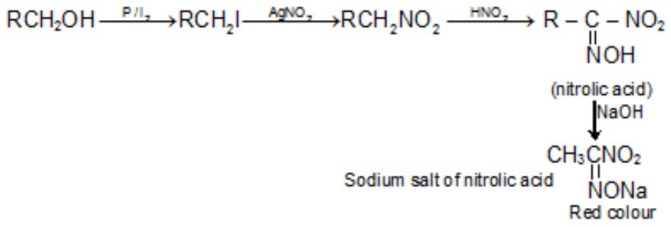
Phenol:

- 2^0 Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5-10 min.
- 3^0 Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ white turbidity instantaneously.

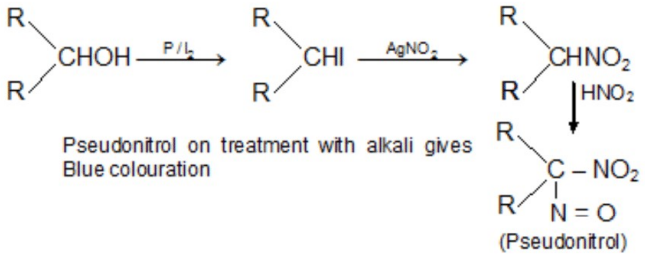
2. Victor Meyer Test

1° alcohol:

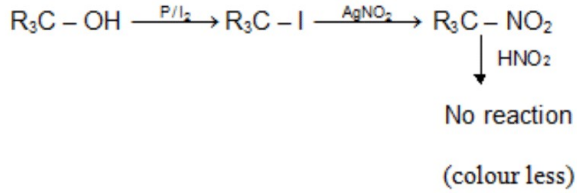


Nitrolic acid on treatment with alkali gives colouration

2° alcohol:



3° alcohol:



Phenols:

Preparation:

- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is, steam volatile and also is less soluble in water because of intramolecular hydrogen bonding

Chemical Properties of Phenols

a) Formation of Esters

Phenyl esters (RCOOAr) are not formed directly from RCOOH. Instead, acid chlorides or anhydrides are reacted with ArOH in the presence of strong base

$(CH_3CO)_2O + C_6H_5OH + NaOH \rightarrow CH_3COOC_6H_5 + CH_3COONa + H_2O$

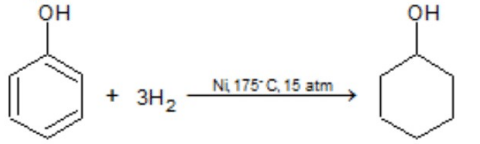
Phenyl acetate

$C_6H_5COCl + C_6H_5OH + NaOH \rightarrow C_6H_5COOC_6H_5 + Na^+Cl^- + H_2O$

Phenyl benzoate

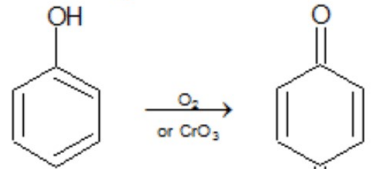
b) Displacement of OH group: $ArOH + Zn \xrightarrow{\Delta} ArH + ZnO$ (poor yields)

c) Hydrogenation



cyclohexanol

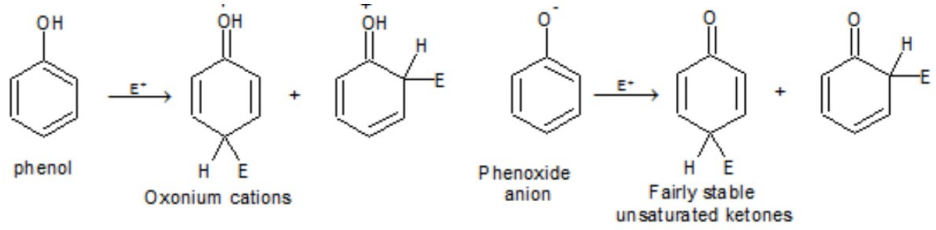
d) Oxidation to Quionones



phenol

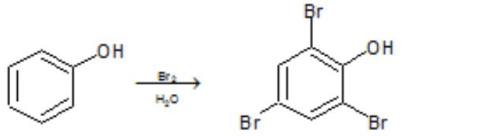
benzo-1,4-quinone

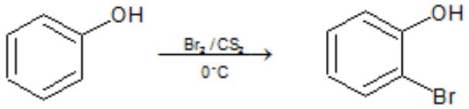
e) Electrophilic Substitution The —OH and even more so the —O(phenoxide) are strongly activating ortho ,para - directing



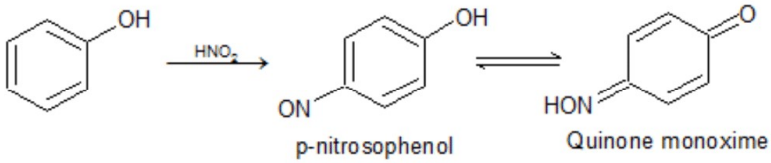
Special mild conditions are needed to achieve electrophilic monosubstituion in phenols because their high reactivity favors both polysubstitution and oxidation

f) Halogenation

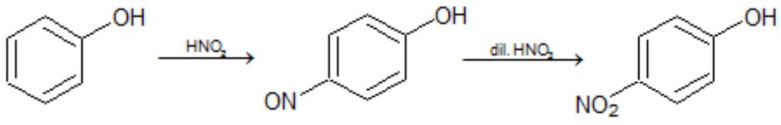




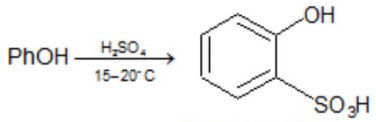
h) Nitrosation



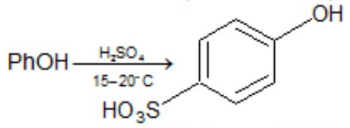
i) Nitration



j) Sulfonation



(rate-controlled)



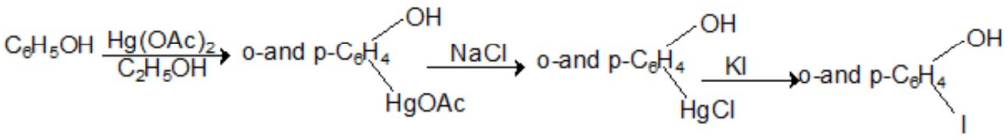
(eqbm-controlled)

k) Diazonium salt coupling to form azophenols

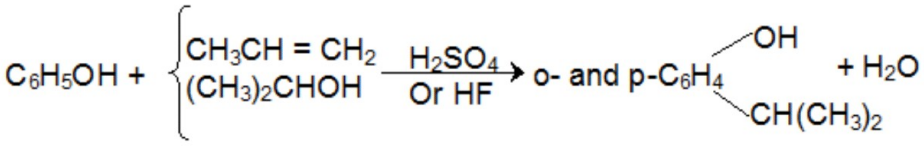
Coupling (G in ArG is an electron – releasing group)

$ArN_2^+ + C_6H_5G \longrightarrow p\text{-}G—C_6H_4—N=N—Ar$ (G = OH, NR_2, NHR, NH_2)

l) Mercuration

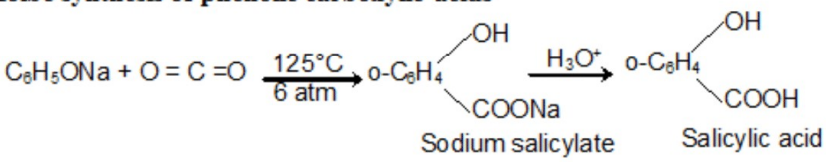


m) Ring alkylation



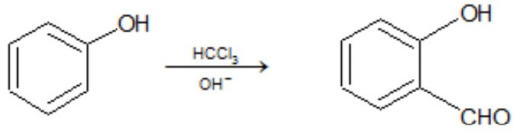
RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O.

n) Kolbe synthesis of phenolic carboxylic acids



Phenoxide carbanion adds at the electrophilic carbon of CO_2, para product is also possible.

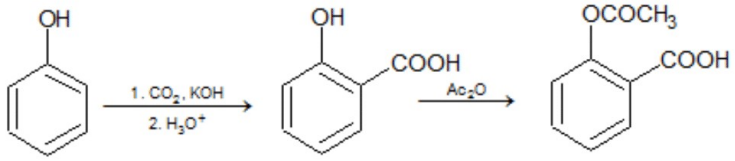
o) Reimer – Tiemann synthesis of phenolic aldehydes



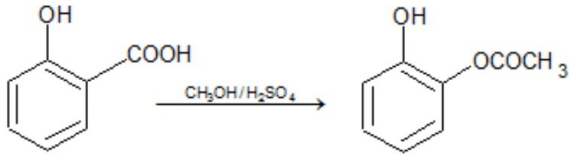
The electrophile is the dichlorocarbene, $:CCl_2$, formation of carbene is an example of α-elimination. $\overline{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)

a)



b)



Ethers:

Physical Properties of Ethers