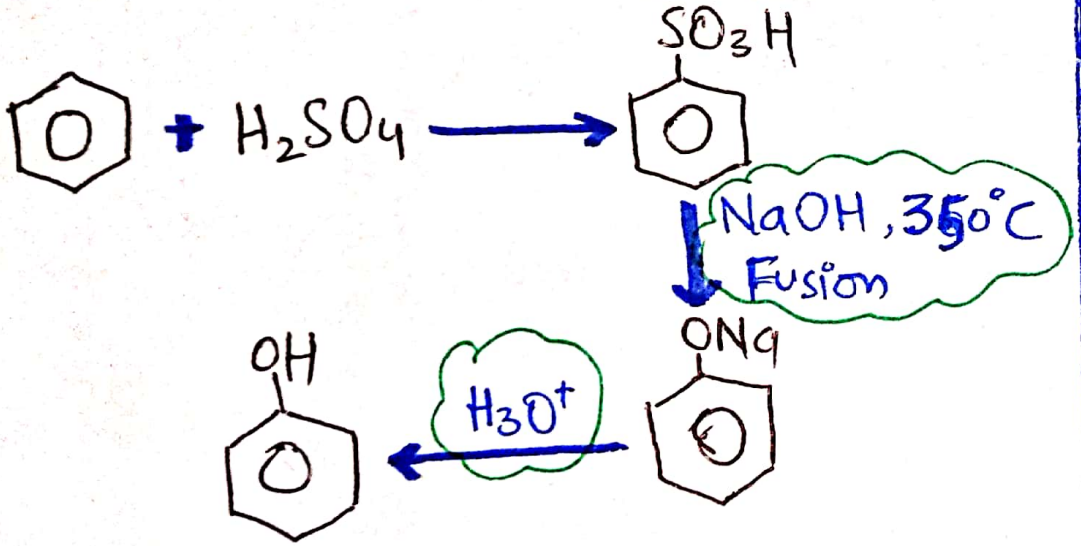
PHENOLS

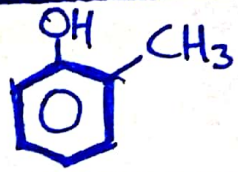
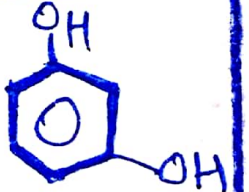
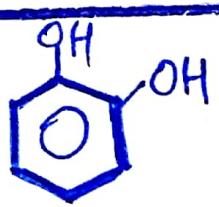
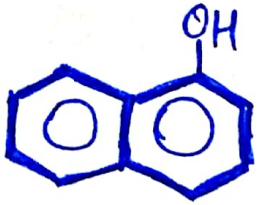
- Hydroxybenzene.

PREPATORY METHODS

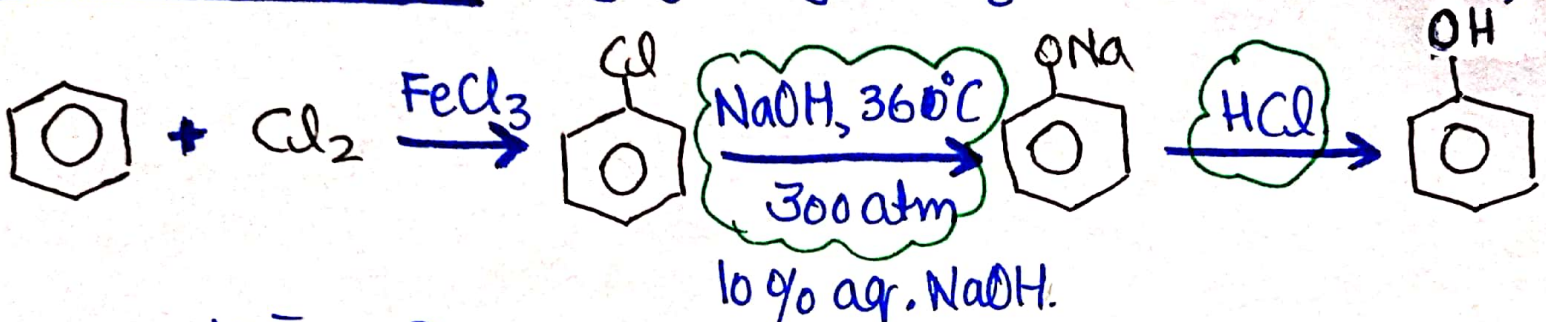
1. Fusion of sodium benzenesulfonate with alkali



- Method used in laboratories mixture of KOH and NaOH are used.

	Phenol
	o-cresol
	Hydroquinone.
	Resorcinol
	Catechol.
	α-Naphthol

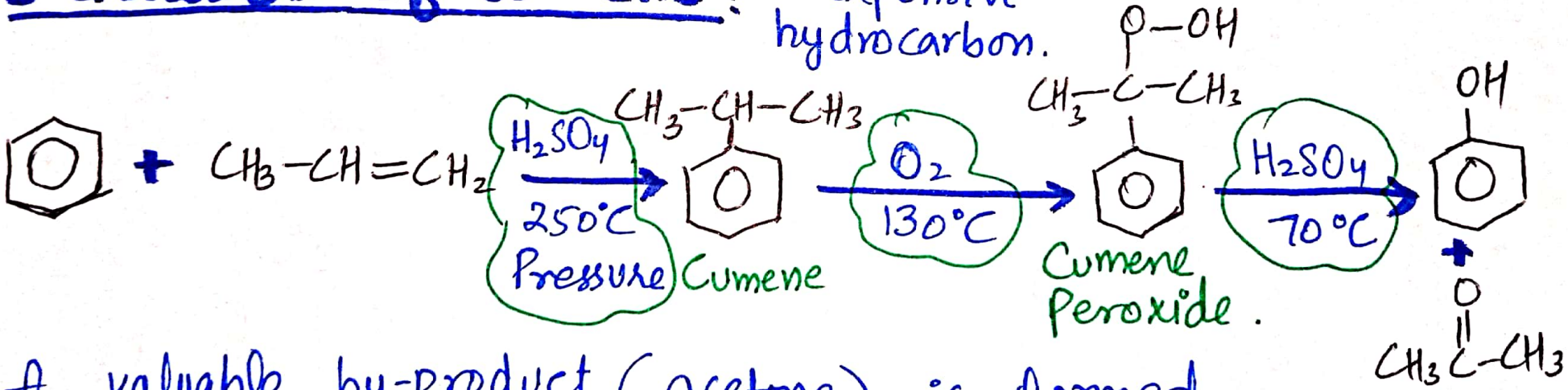
2. Dow's Method (Hydrolysis of chlorobenzene)



- Intermediate = Benzyne

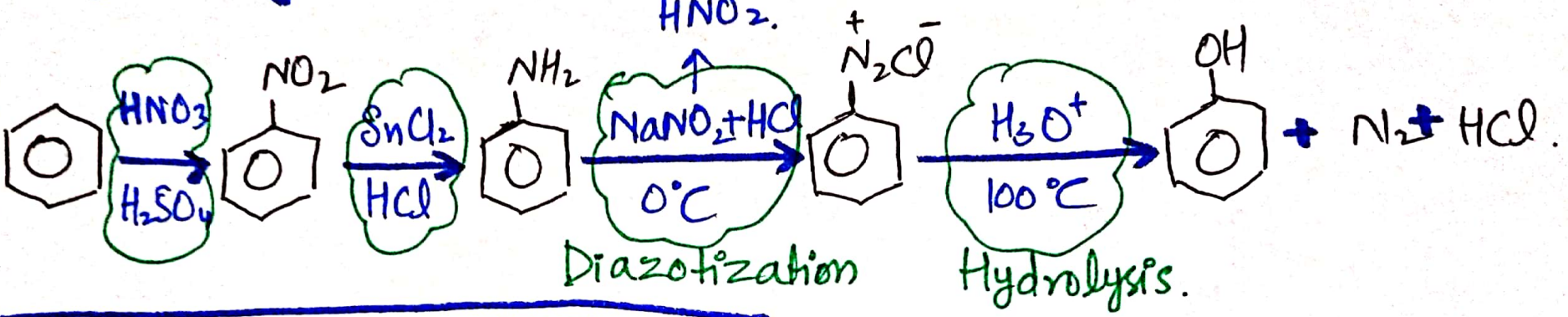
- Not suitable in laboratories — Isomeric products formed.

3. Oxidation of cumene → inexpensive hydrocarbon.



- A valuable by-product (acetone) is formed
- Today, whole of the Phenol is formed by this method.

4. Hydrolysis of Aryl diazonium salts:



PHYSICAL PROPERTIES

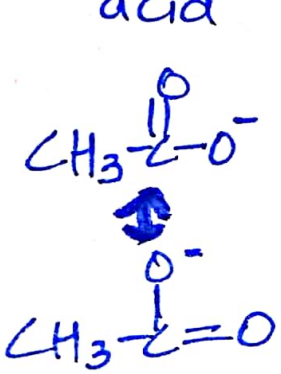
- Monohydric phenols — either liquid or low melting crystalline solids.
- Have distind odour.
- Generally colorless — unless some chromophore present on molecule.
- Phenol easily oxidized by air

- M.P° = 41°C
- B.P° = 182°C

- Completely soluble in water at 68.5°C
- Poisonous.

- $K_a = 1.3 \times 10^{-10}$
- Order of acidity = Carboxylic acid > Phenol > Water > Alcohol

conjugate bases:



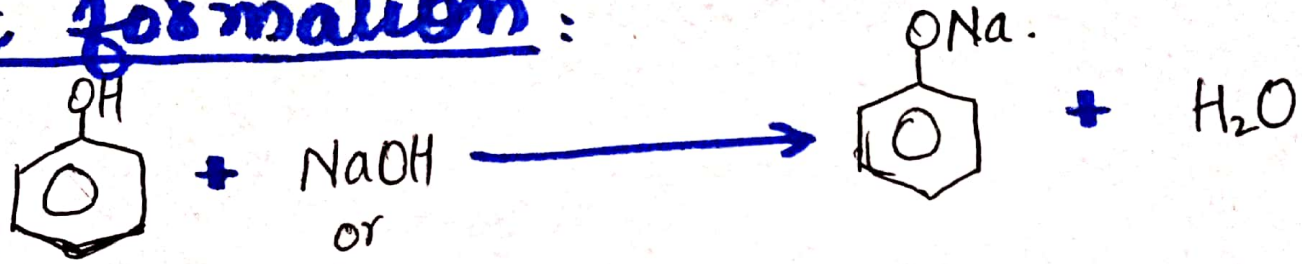
$\bar{O}H$ RO^-

- Electron withdrawing group on benzene ring increases acidity of phenol.

CHEMICAL REACTIONS

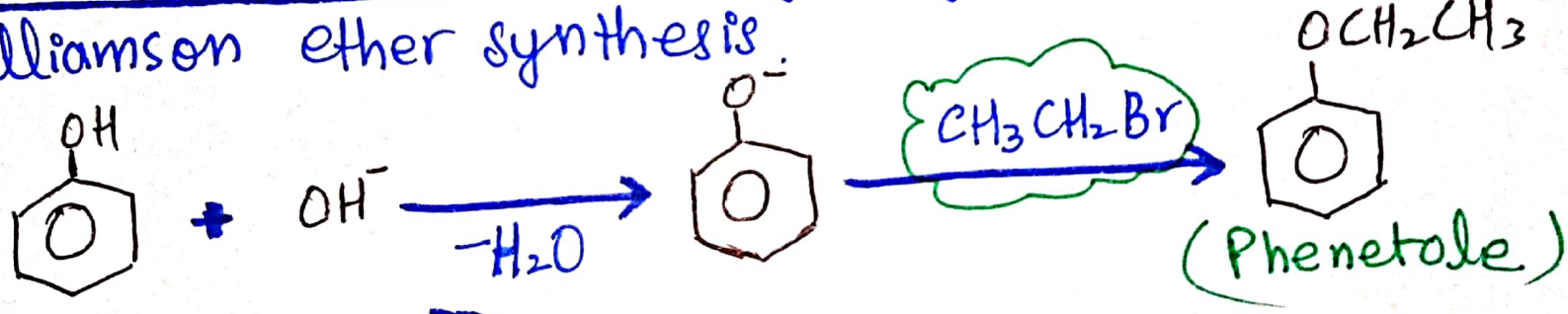
- Give Electrophilic Substitution reactions
- Act as acid.

1- Salt formation:

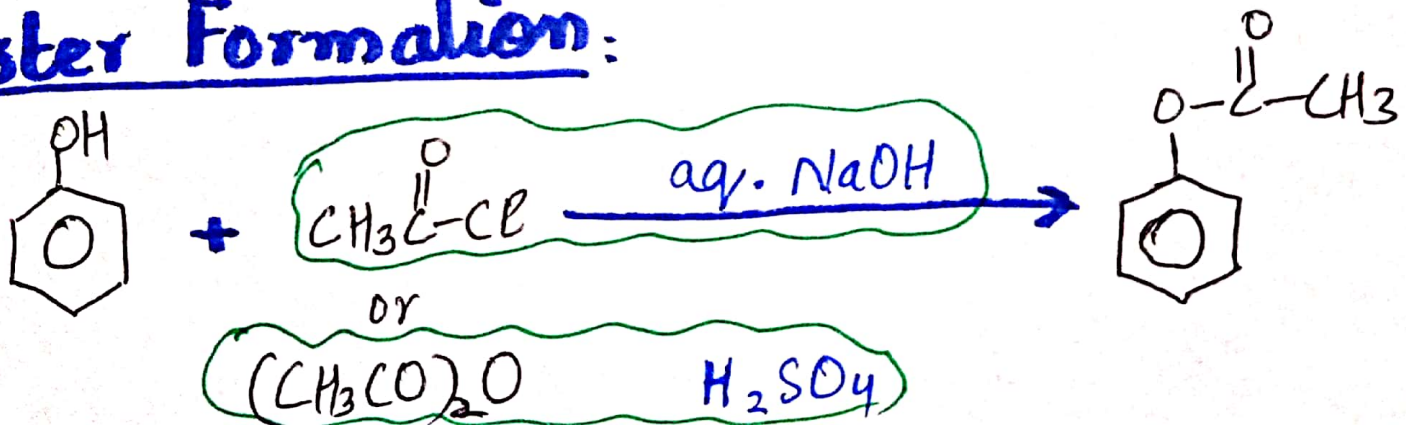


2- Ether Formation: (AlRyl Aryl Ether)

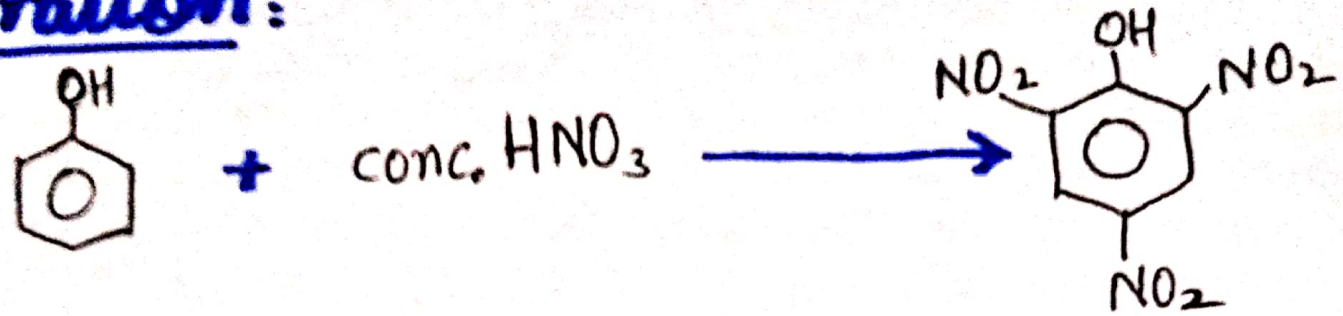
- Williamson ether synthesis.



3- Ester Formation:

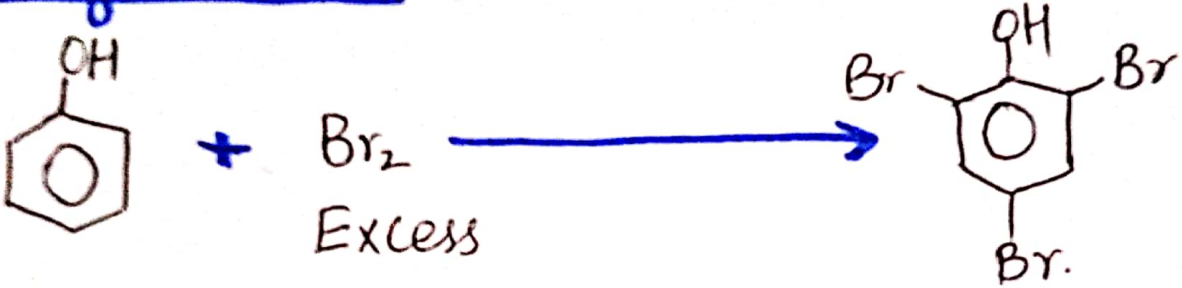


4. Nitration:

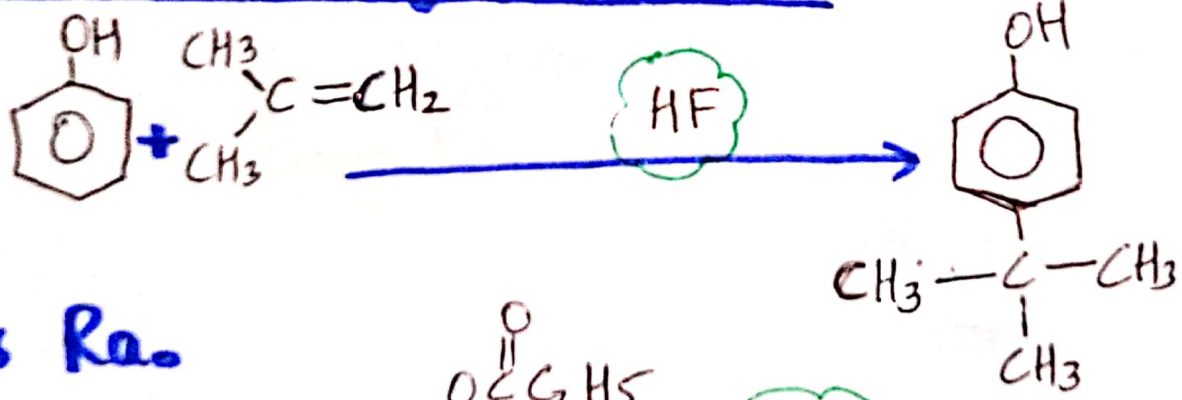


Picric acid.

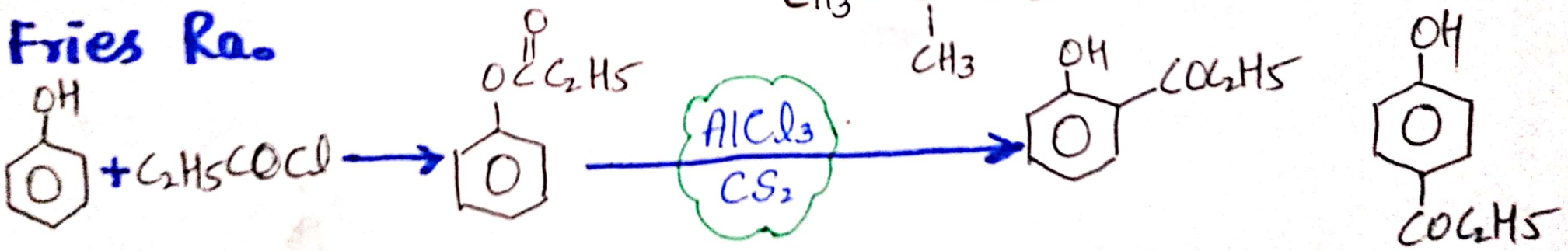
5. Halogenation:



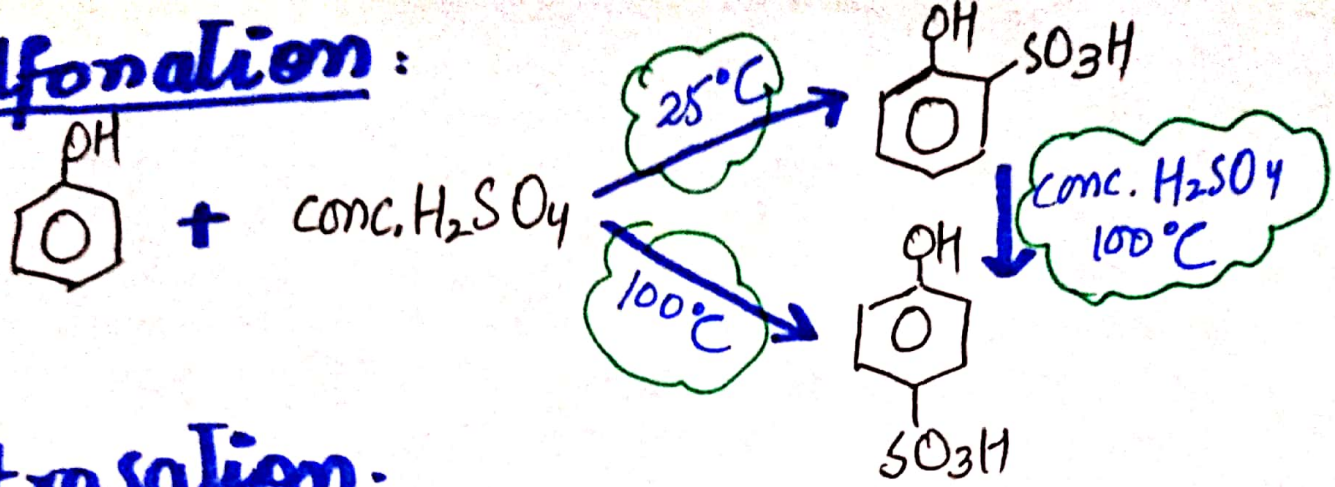
6. Friedal Craft Reaction:



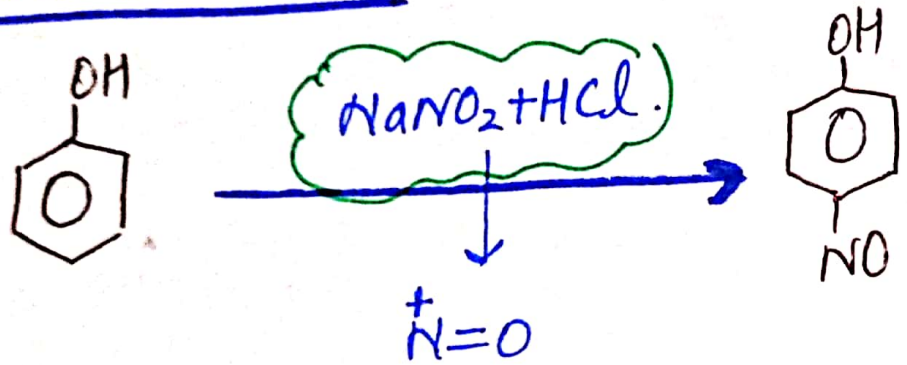
• Fries Re.



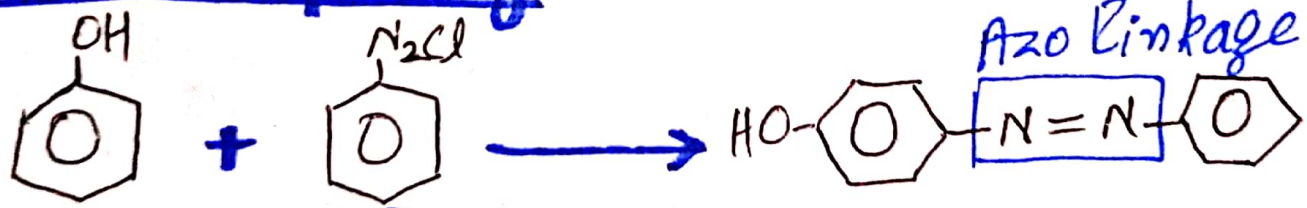
7. Sulfonation:



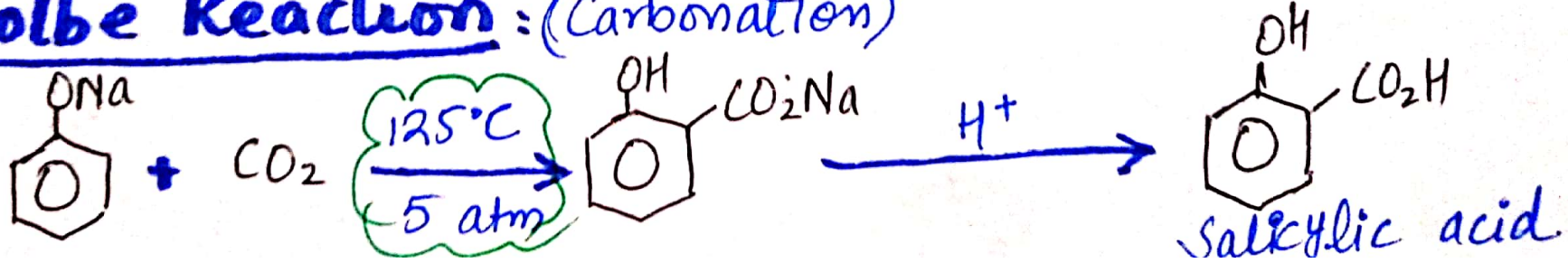
8. Nitrosation:



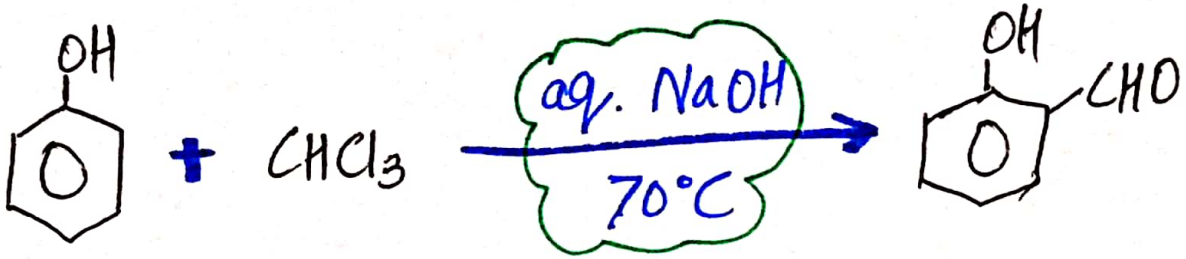
9. Diazo coupling:



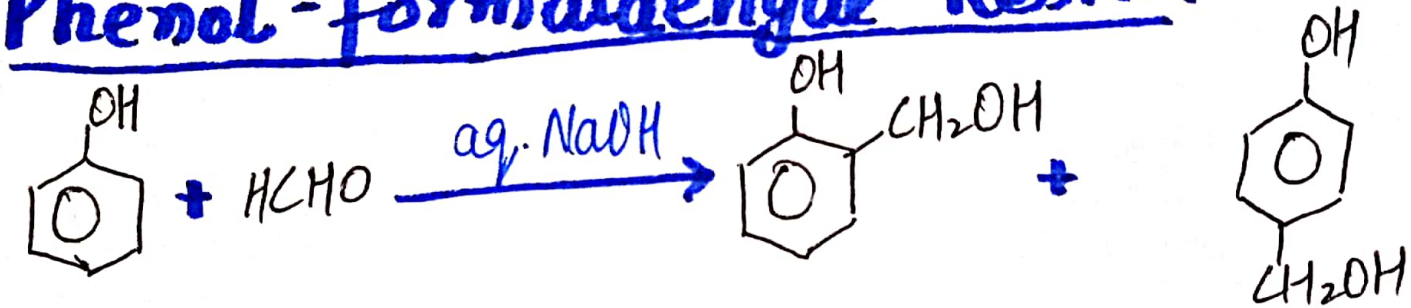
10. Kolbe Reaction: (Carbonation)

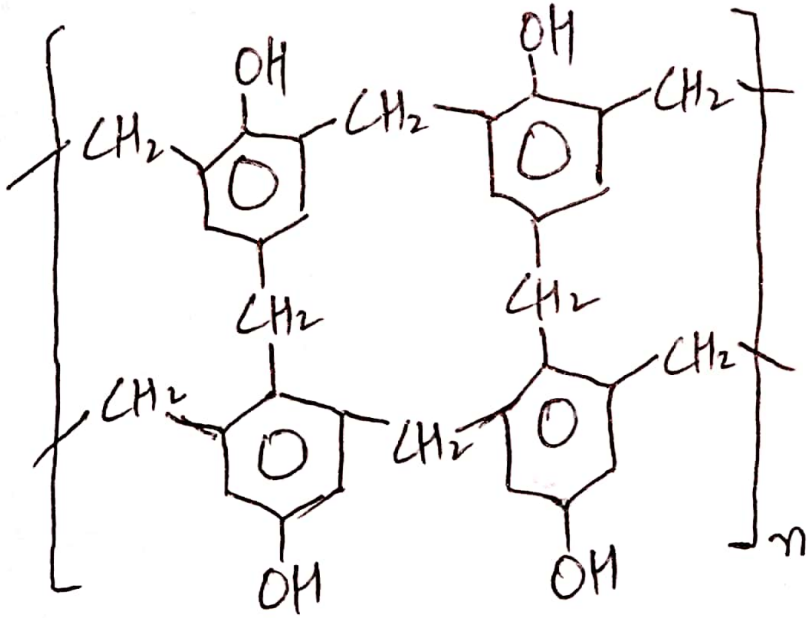


11. Reimer Tiemann Reaction : (Formylation)



12. Phenol-formaldehyde Resin :

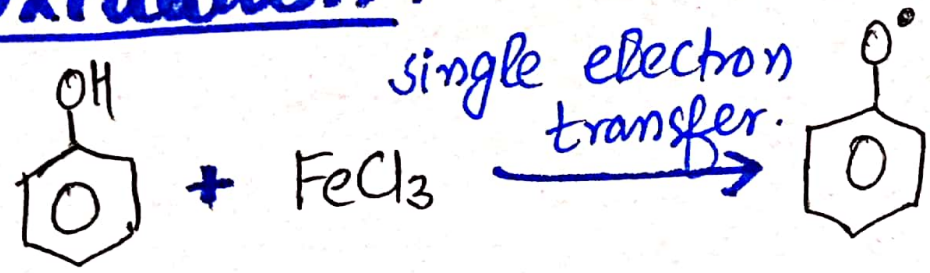


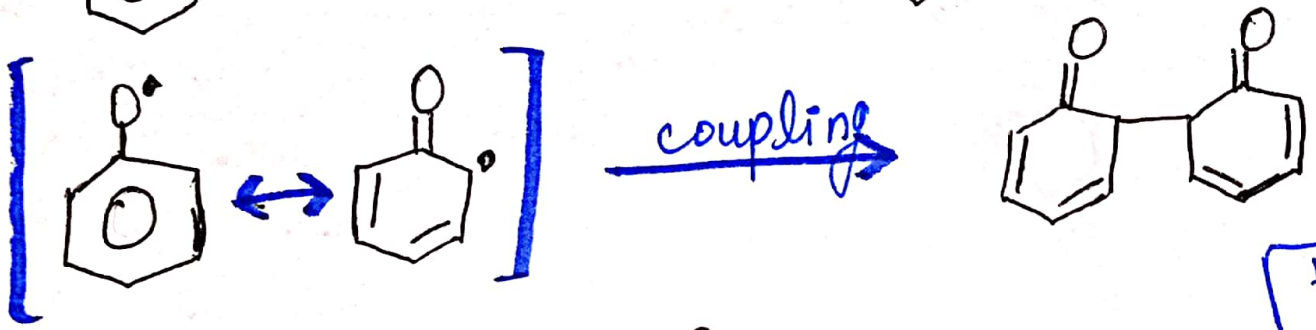


Bakelite.
(Thermoset Resin)

- to make electric shoes, plugs etc.

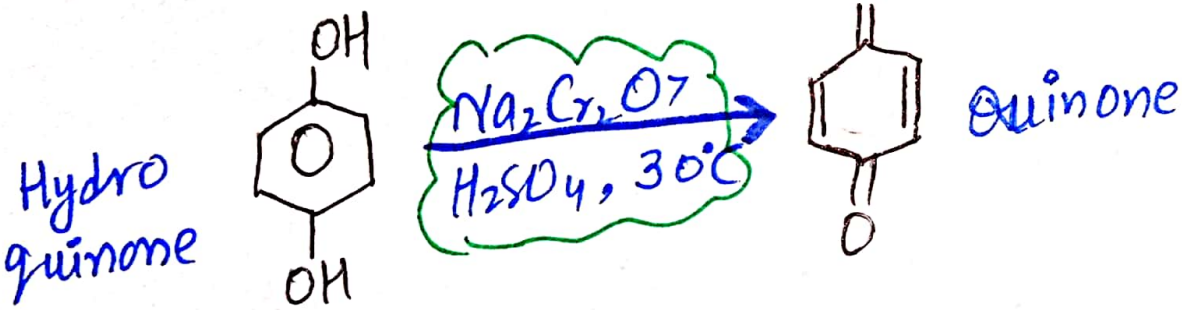
13. Oxidation:



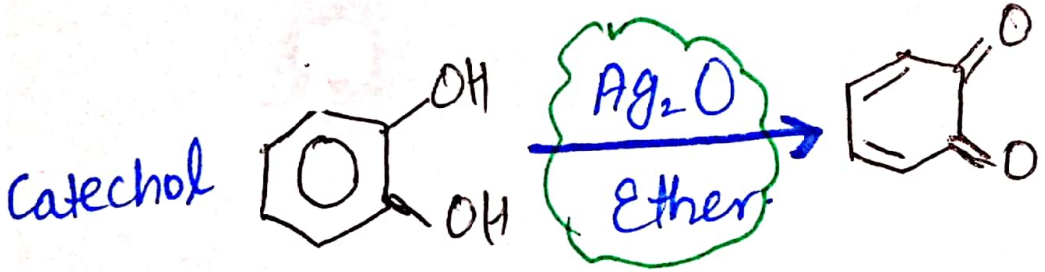


- Test for identification
  - violet
  - ↓
  - Blue
  - ↓
  - Green
  - ↓
  - Red.

Formation of ferric phenoxide



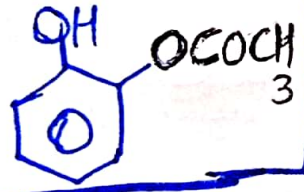
- Hydroquinone = photographic developer.



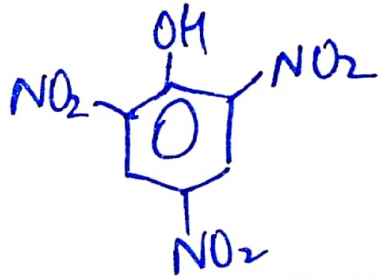
Uses :-

- Phenolic ethers present in essential oils.
- Important industrial material.
- Used to produce important Commecial products

Aspirin



Picric Acid



ETHERS

- Derivative of water
- R-O-R Dialkyl ethers.
- Symmetrical or unsymmetrical
- $C_nH_{2n+2}O$, similar to monohydric alcohol.

Used as anesthetic and as solvent.

-  Anisole
-  Phenetole

PREPARATORY METHOD

1. Dehyration

- Intermolecular dehydration of alcohol.

$$CH_3CH_2OH + HOCH_2CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

- Symmetrical ethers formed
- This reaction competes with elimination.
- SN2 mechanism. (Substrate = Protonated form of alcohol)
- Commercial method.

2. Williamson ether Synthesis:

- to synthesize symmetrical or unsymmetrical ethers. (SN2)

$$2\,CH_3CH_2OH + 2Na \longrightarrow 2\,CH_3CH_2\bar{O}Na + H_2$$

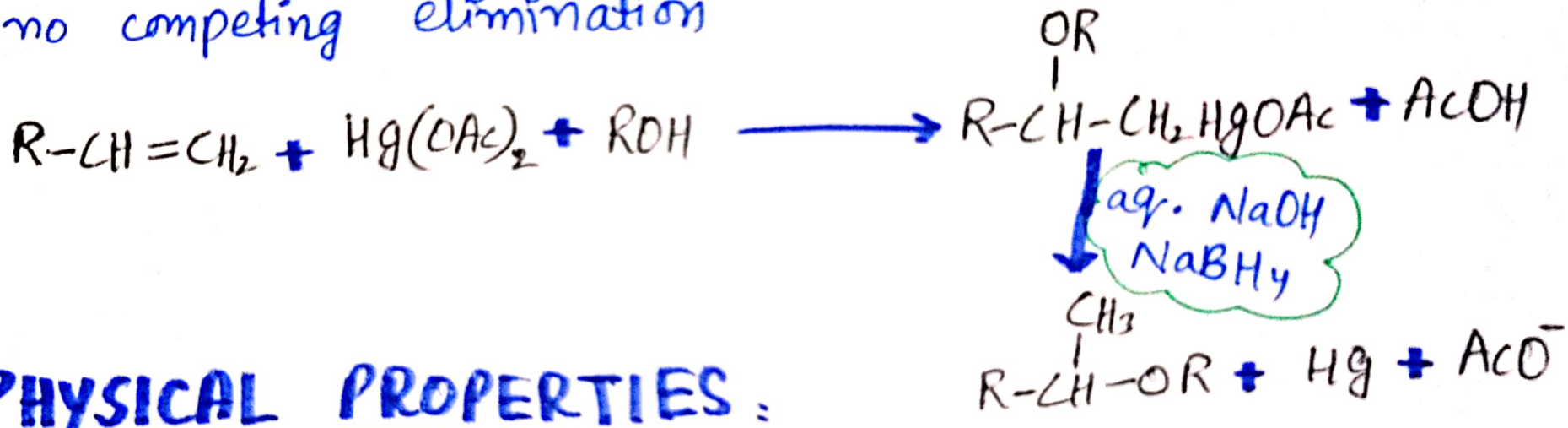
$$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$$

$$CH_3CH_2Cl + 2\,CH_3CH_2\bar{O}Na \longrightarrow CH_3CH_2OCH_2CH_3 + NaCl$$

- Primary alkyl sulfate $((RO)_2SO_2)$ or sulfonates $(ROSO_2R)$ may be used as substrate.

3. Alkoxymercuration- demercuration

- From alkene.
- no competing elimination



PHYSICAL PROPERTIES:

- Lower members — either gases or volatile liquids and highly inflammable
- M.P° close to corresponding hydrocarbons
- Donot have H-bonding.
- Less dense than water.
- Soluble in organic solvents

CHEMICAL PROPERTIES

- Relatively inert to most reagents.
- Stable to dil. acids but form oxonium ion with conc. strong acids.
- used as solvents.
- Suseptible to attack by free radicals.

1. Cleavage of ether linkage:

$$R\text{-}O\text{-}R \xrightarrow{\text{conc. } H_2SO_4} ROH + ROSO_3H$$

$$C_2H_5\text{-}O\text{-}C_2H_5 + HI \xrightarrow{57\%} C_2H_5OH + C_2H_5I$$

Ziesel method:

$$R\text{-}O\text{-}CH_3 + HI \longrightarrow ROH + CH_3I$$

weighed ppt.

$$CH_3I + AgINO_3 + C_2H_5OH \longrightarrow C_2H_5OCH_3 + \boxed{AgI} + HNO_3$$

used to determine number of methoxy groups.

2- Auto-oxidation:

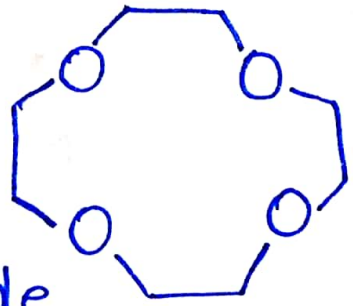
- Slow oxidation in air.
- form hydroperoxides and peroxides (hazardous)
- Free Radical mechanism.
- Shake ether with aq. soln. of KI (color violet changes to red) due to Presence of peroxides.

3- Halogenation:

$$CH_3CH_2OCH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3\underset{\alpha}{C}H(Cl)OCH_2CH_3$$

CROWN ETHER

- 12-crown-4
- can dissolve ionic Compounds ie KF (insoluble in benzene) but soluble in 18-crown-6)
- cyclic polymers of ethylene glycol $+OCH_2CH_2+_n$



- phase transfer catalysts