Organic Compounds Containing Oxygen

Alcohols, Phenols and Ether:

Alcohols

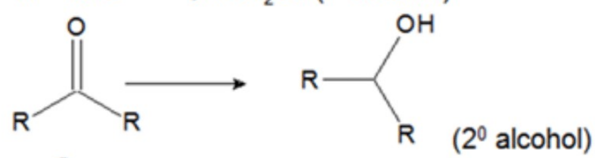
Preparation of Alcohols:

- **By hydrolysis of haloalkanes :** R-X + aq. KOH →ROH +KX
- **By reduction of Carbonyl compounds**

$$4RCOOH + 3LiAlH_4 \rightarrow 4RCH_2OH \ \ (\mathbf{1^o alcohol})$$

$$CH_3(CH_2)_{14}COOC_2H_5 \xrightarrow{LiAlH_4} CH_3(CH_2)_{14}CH_2OH$$

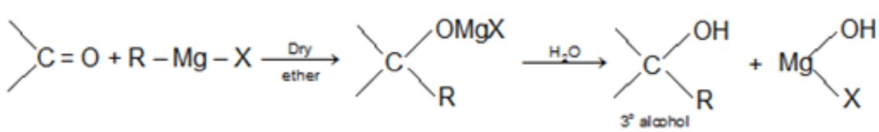
$$R-CHO \longrightarrow RCH_2OH(1^O\ alcohol)$$



$$R-\overset{\overset{O}{||}}{C}-OR' \xrightarrow{4[H]} R-CH_2OH + R'OH$$

$$CH_3CH_2COOCH_3 \xrightarrow{Cr_2O_4} CH_3CH_2CH_2OH + CH_3OH$$

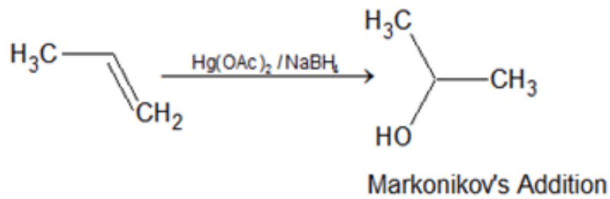
- **By the action of Grignard's Reagent on aldehydes, ketones and esters**



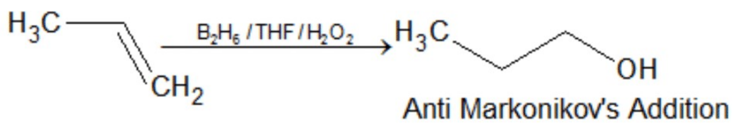
- **By Aliphatic Primary Amines: RCH_2NH_2 + HNO_2 → RCH_2OH + N_2 + H_2O**
- **Hydration of alkenes:**

$$CH_2 = CHR + \underset{Concentrated}{H_2SO_4} \xrightarrow[H_2O]{Boil} CH_3 - CH(R)OH$$

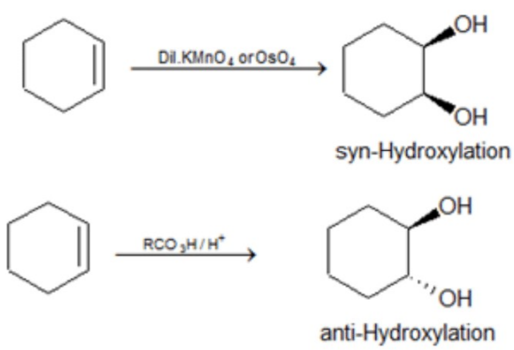
- **Oxymercuration-demercuration:**



- **Hydroboration-oxidation:**



- **Hydroxylation of alkenes:**

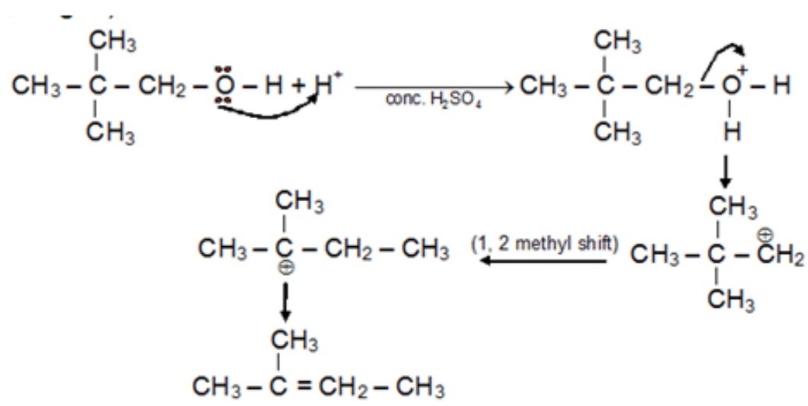


Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

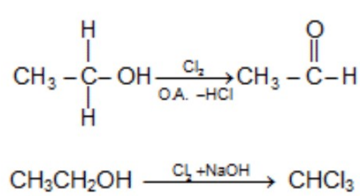
Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:** $ROH + Na \rightarrow 2RO^{+}Na^{-} + H_2$
- **Formation of Halides:**
  - $3ROH + P + I2 \rightarrow 3RI + H_3PO_3$
  - $ROH + SOCl_2/PCl_3/PCl_5 \rightarrow RCl$
  - $ROH + HX \rightarrow RX$
  - $ROH + NaBr, H_2SO_4 \rightarrow R\text{-}Br$
  - $ROH + Zn + HCl \rightarrow R\text{-}Cl$
  - $R_2C\text{-}OH$ alcohol + $HCl \rightarrow R_2CCl$
- **Reaction with HNO_3:** $R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$
- **Reaction with carboxylic acid (Esterification) :** $R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$
- **Reaction with Grignard reagent:** $R'OH + RMgX \rightarrow RH + R'OMgX$
- **Reduction of alcohol :** $ROH + 2HI$ + Red P $\rightarrow RH + I_2 + H_2O$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: $3° > 2° > 1$
- **Satyzeff's Rule :** Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol**:
  RCH_2-OH + [O] → RCHO → RCOOH
  RCH_2-OH + [O] +PCC → RCHO

- **Haloform Reaction:** Compound containing CH_3CO- group (or compound on oxidation gives CH_3CO – group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.CH_3-CH_2-$COCH_2$-CH_3, CH_3-CO-Cl, CH_3COOH will not respond to haloform reaction wile CH_3CH_2OH will respond to haloform Reaction.
  ?



Test for Alcohols:

1. Lucas Test:

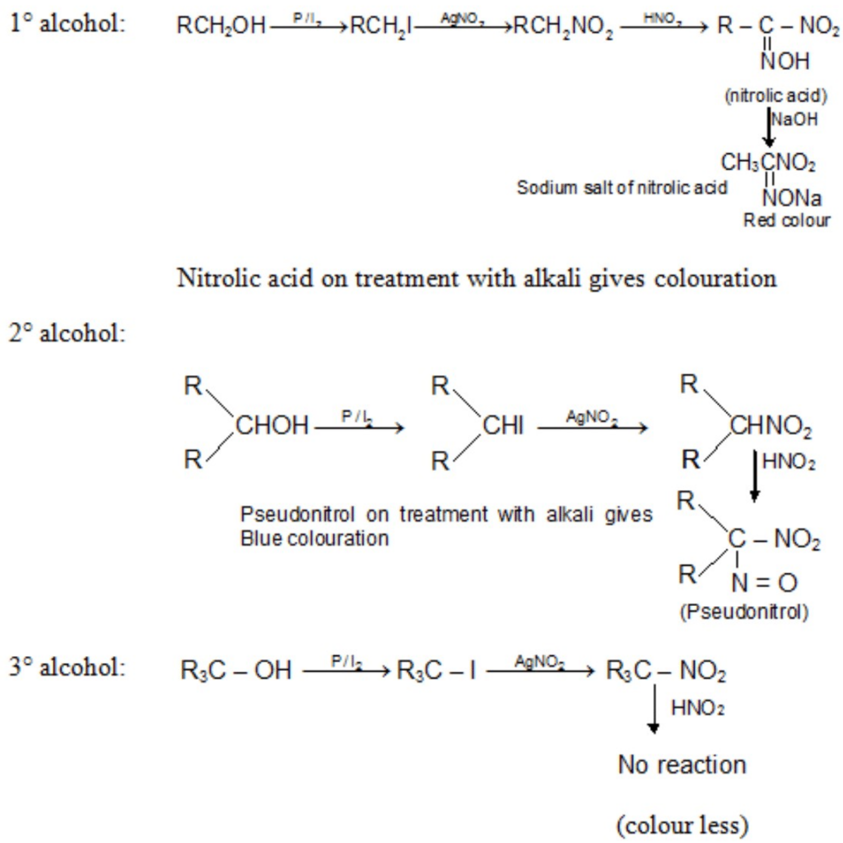
Alcohols + $ZnCl_2$ + HCl

- 1° Alcohol: RCH_2OH + $ZnCl_2$ +HCl → No reaction at room temperature

- 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.

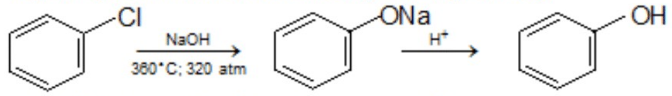
2. Victor Meyer Test



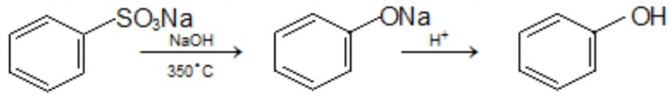
Phenols:

Preparation:

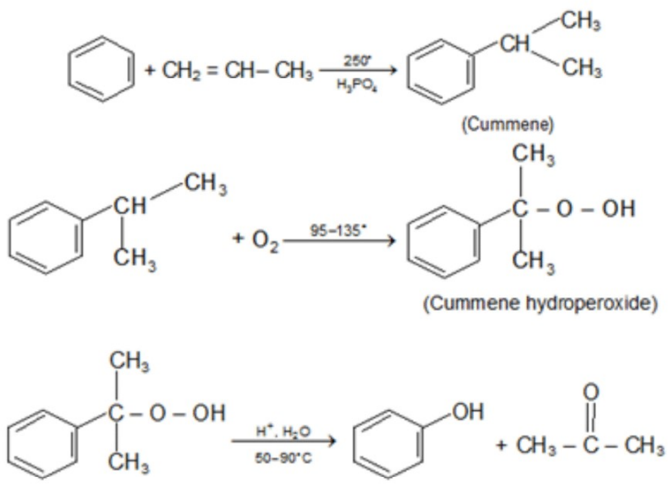
a. **Hydrolysis of chlorobenzene: (Dow's process)**



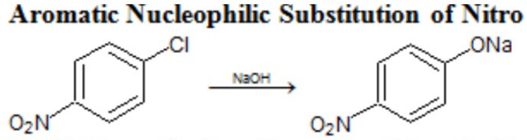
b. **Alkali fusion of Sodium benzene sulfonate**



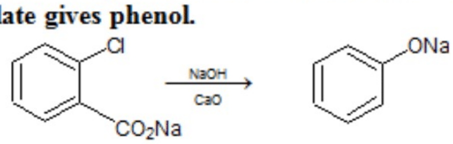
c. **From Cummene Hydroperoxide**



d. **Aromatic Nucleophilic Substitution of Nitro Aryl Halides**



e. **Distillation of phenolic acids with soda-lime produces phenols, e.g. sodium salicylate gives phenol.**



Physical Properties of Phenols

- Phenol is a colorless, toxic, corrosive, needle shaped solid.
- Phenol soon liquifies due to high hygroscopic nature.
- Phenol is less soluble in water, but readily soluble in organic solvents.

- 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

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

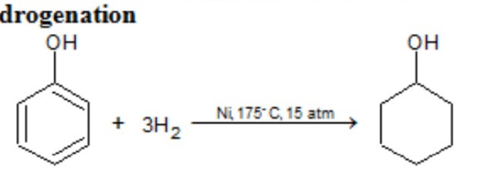
Phenyl acetate

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

Phenyl benzoate

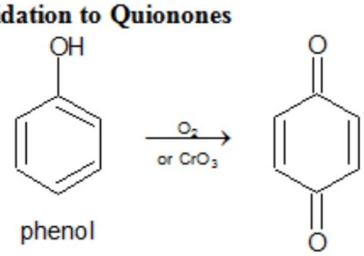
b) Displacement of OH group: $ArOH + Zn \xrightarrow{\Delta} ArH + ZnO$ (poor yields)

c) Hydrogenation



cyclohexanol

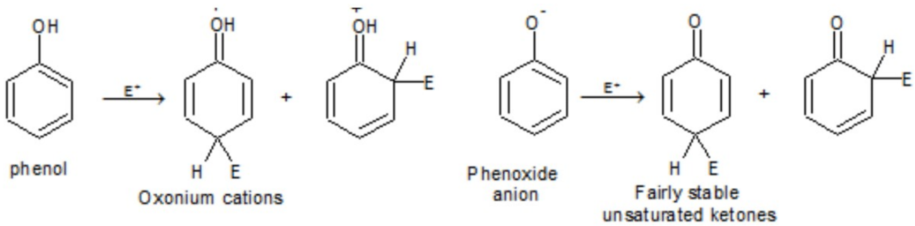
d) Oxidation to Quionones



phenol

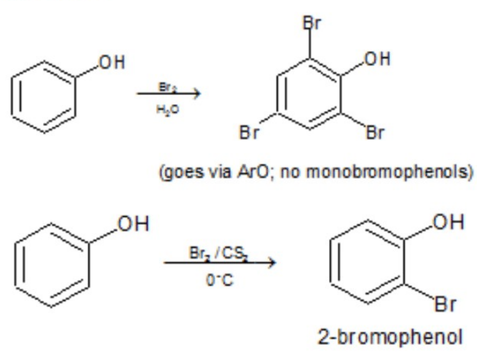
benzo-1,4-quinone

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

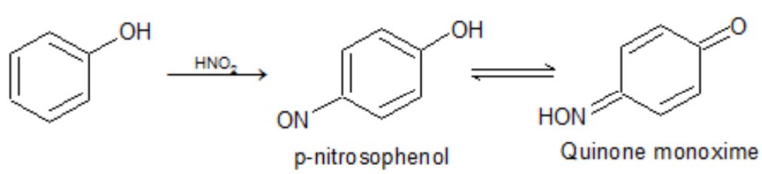


Special mild conditions are needed to achieve electrophilic monosubstituion in phenols because their high reactivity favors both polysubstitution and oxidation

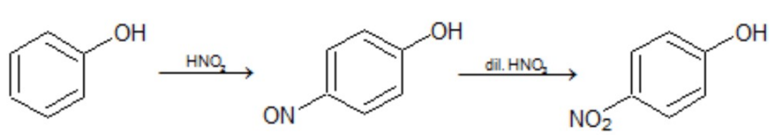
f) Halogenation



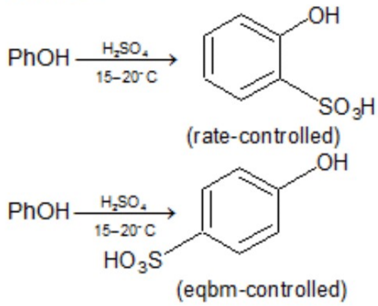
h) Nitrosation



i) Nitration



j) Sulfonation

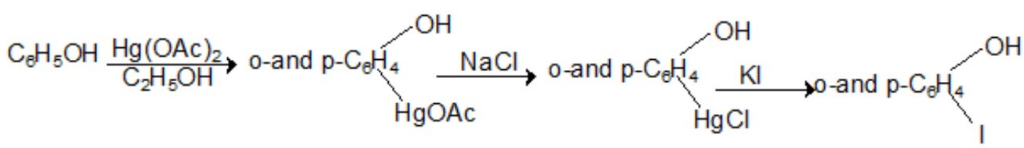


k) Diazonium salt coupling to form azophenols

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

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

l) Mercuration



m) Ring alkylation

$$C_6H_5OH + \begin{cases} CH_3CH = CH_2 \\ (CH_3)_2CHOH \end{cases} \xrightarrow[\text{Or HF}]{H_2SO_4} \text{o- and p-}C_6H_4 \begin{matrix} OH \\ CH(CH_3)_2 \end{matrix} + H_2O$$

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

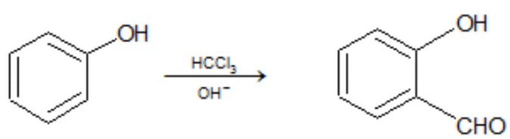
n) Kolbe synthesis of phenolic carboxylic acids

$$C_6H_5ONa + O = C = O \xrightarrow[6\ atm]{125°C} \text{o-}C_6H_4 \begin{matrix} OH \\ COONa \end{matrix} \xrightarrow{H_3O^+} \text{o-}C_6H_4 \begin{matrix} OH \\ COOH \end{matrix}$$

Sodium salicylate   Salicylic acid

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

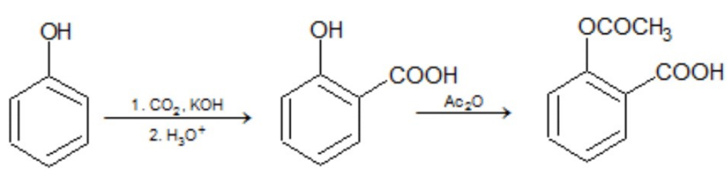
o) Reimer – Tiemann synthesis of phenolic aldehydes



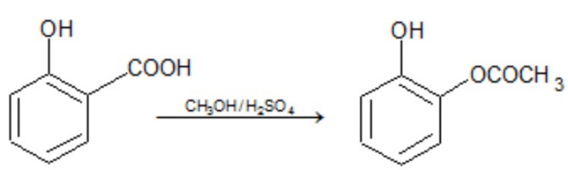
The electrophile is the dichlorocarbene, $:CCl_2$, formation of carbene is an example of α-elimination. $\overline{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

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

a)



b)

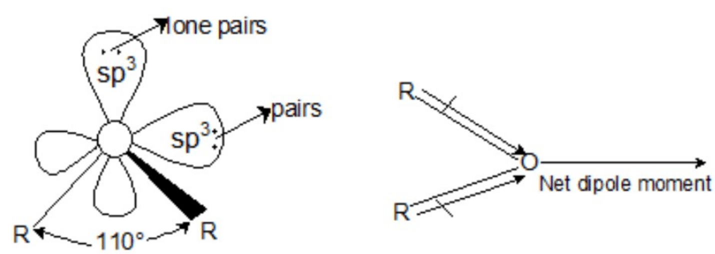


Ethers:

Physical Properties of Ethers

- **Physical state, colour and odour**: Dimethyl ether and ethyl methyl ether is gas at ordinary temperature while the other lower homologues of ethers are colourless liquid with characteristic 'ether smell'.

- **Dipole nature**: Ethers have a tetrahedral geometry i.e., oxygen is sp^3 hybridized. The C— O—C angle in ethers is 110°. Because of the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.



  Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

- **Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

Preparation of Ethers:

a) From alcohols:

$$CH_3CH_2OH \xrightarrow[140^\circ C]{H_2SO_4} \underset{\text{Ether}}{CH_3CH_2-O-CH_2CH_3}$$

Order of dehydration of alcohol leading to formation of ethers: 1° > 2° > 3°

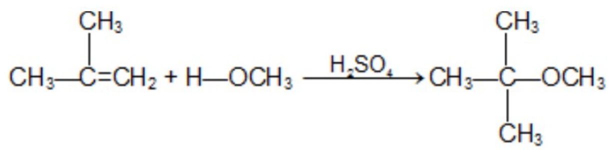
$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2{-}O{-}CH_3 + N_2$$

b) **Williamson's synthesis:**

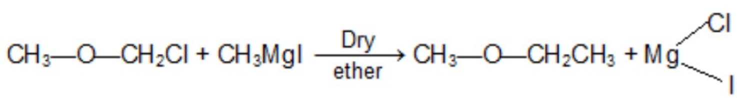
R-X + Na^{+} $^{-}$O-R' → R-O-R' + Na^{+} X^{-}

In case of tertiary substrate elimination occurs giving alkenes.

From alkenes:.



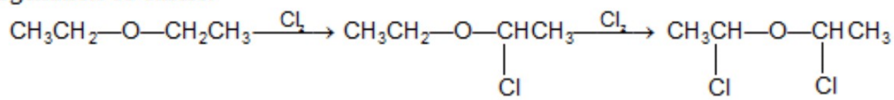
From Grignard reagent: Treating a - halo ethers with suitable Grignard reagents.



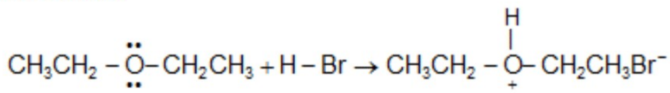
On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate ?

$$\text{Peroxide} + Fe^{2+} \rightarrow Fe^{3+} \xrightarrow{SCN^-} \underset{\text{Red}}{Fe(SCN)_n^{(3-n)-}} \ (n = 1 \text{ to } 6)$$

f) Halogenation of ethers:



g) Ethers as base:



h) Reaction With Cold conc. HI/HBr:

$$R—O—R' + \text{Cold HI} \longrightarrow R\text{-}OH + R'I\ (R' < R)$$

i) Hot conc. HI/HBr:

$$R—O—R' + \text{Hot HI} \longrightarrow RI + R'I + H_2O$$