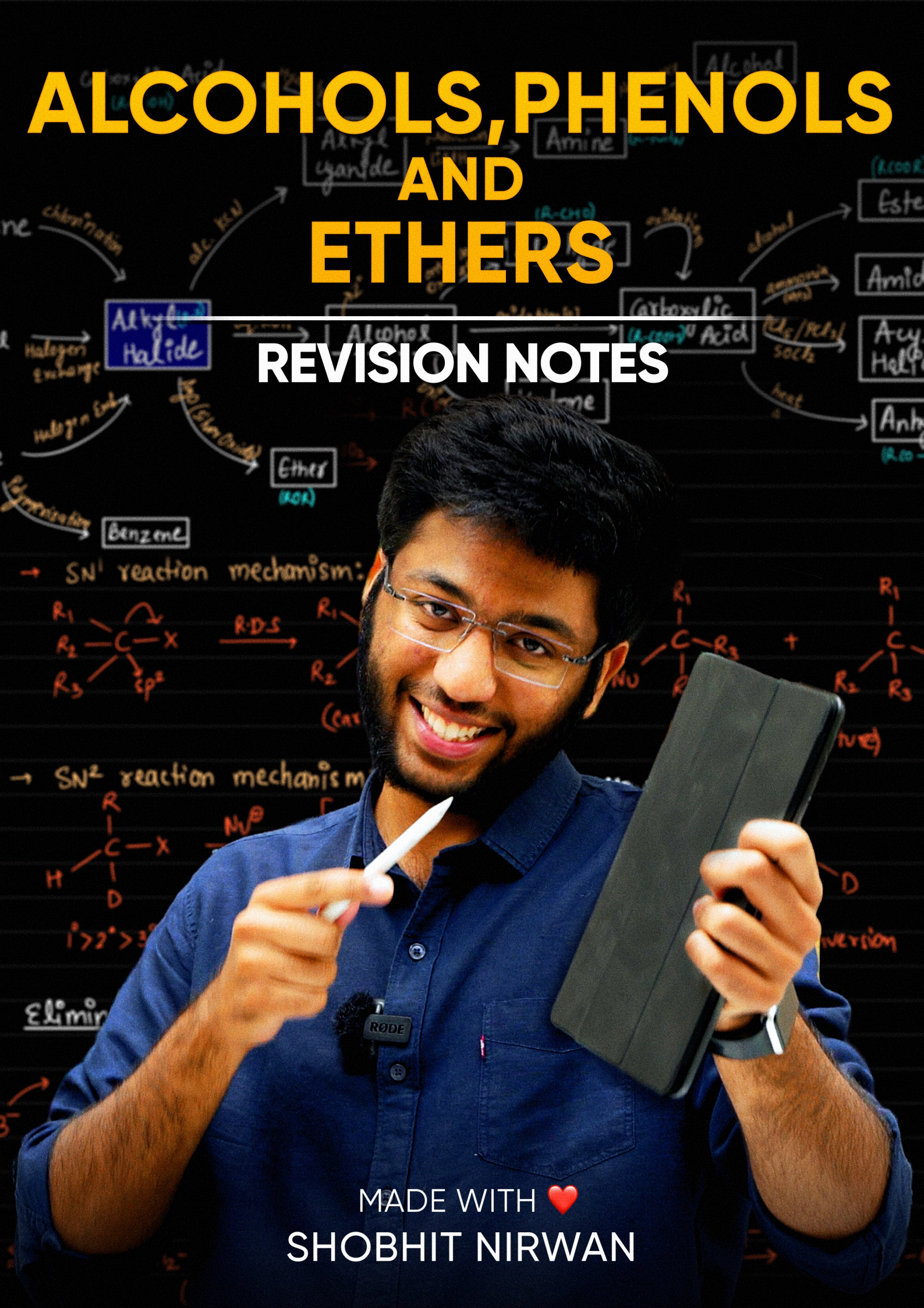
ALCOHOLS, PHENOLS AND ETHERS

REVISION NOTES

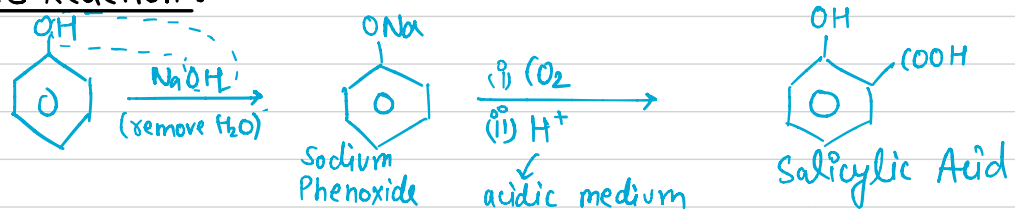


MADE WITH ❤️

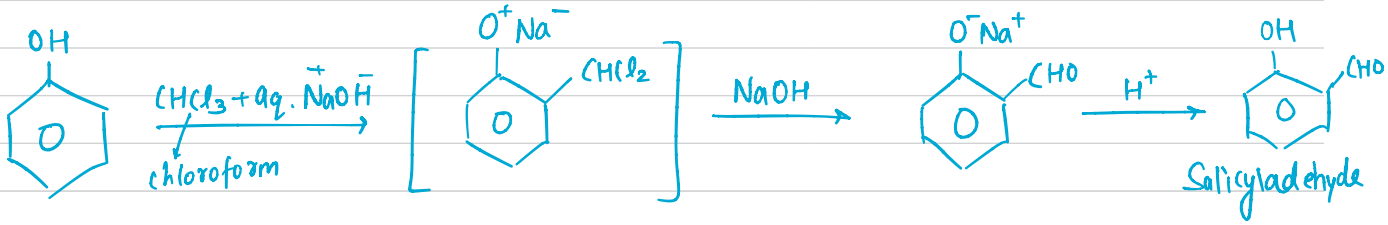
SHOBHIT NIRWAN

NAME REACTIONS OF THIS CHAPTER

(1) Kolbe's Reaction:



(2) Reimer – Tiemann Reaction:



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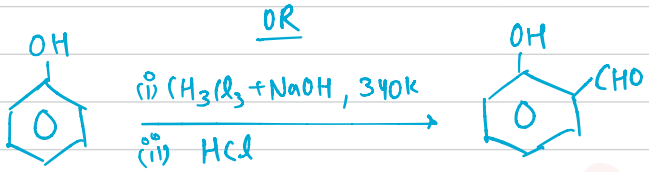
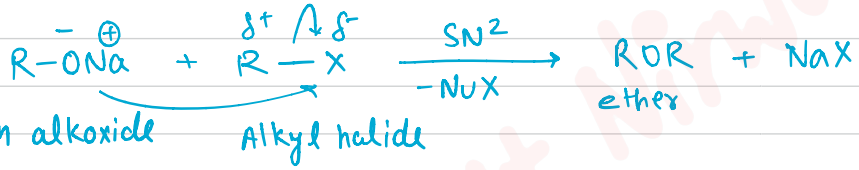
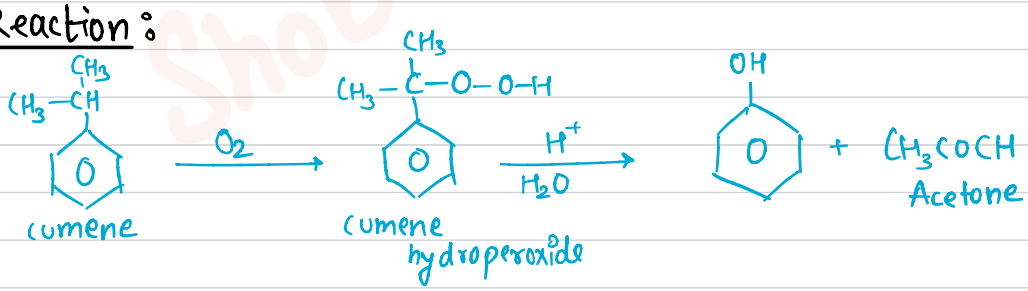


(3) Williamson Synthesis:



eg: $CH_3ONa + CH_3CH_2Br \xrightarrow{-NaBr} CH_3-O-CH_3-CH_2$

(4) Cumene Reaction:

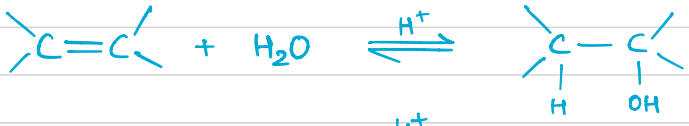


PREPARATIONS

Alcohols

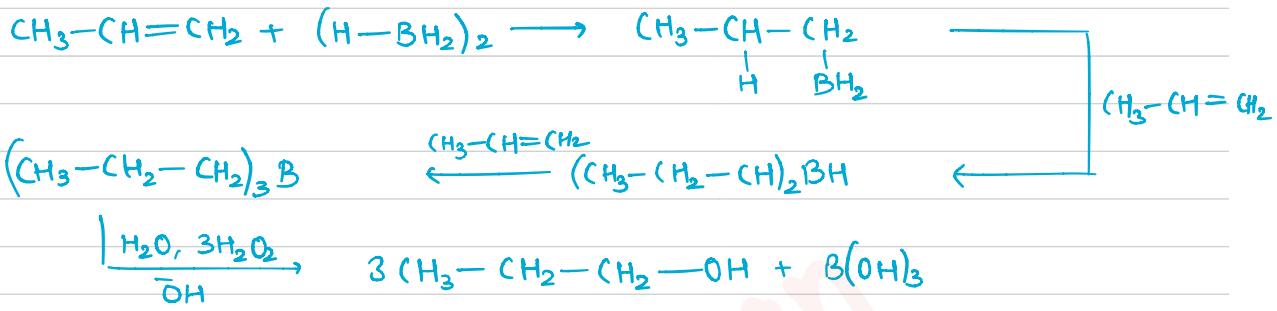
(1) from Alkene:

→ By Acid Catalysted hydration:



eg: $CH_3CH=CH_2 + H_2O \xrightleftharpoons{H^+} CH_3-\underset{OH}{CH}-CH_3$

→ By hydrocarboration oxydation:



(2) from Carbonyl Compounds:

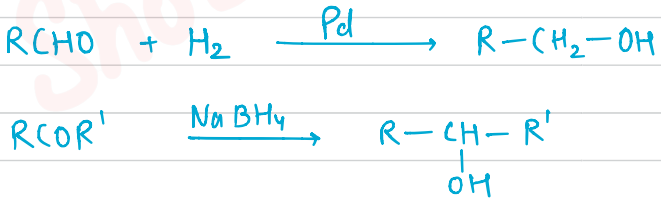
→ By reduction of Aldehydes and ketones:

Addⁿ of H^+ in presence of Catalyst like Pt, Pd, Ni, $NaBH_4$, $LiAlH_4$.

It is expensive, so used for some only

Aldehyde give ⟶ 1° alcohol

Ketone give ⟶ 2° alcohol



K³B: We can get alcohol from acids also via Esters.

$$RCOOH \xrightarrow[H^\oplus]{R'OH} RCOOR' \xrightarrow[Catalyst]{H_2} RCH_2OH + R'OH$$

(3) from Grignard Reagent:

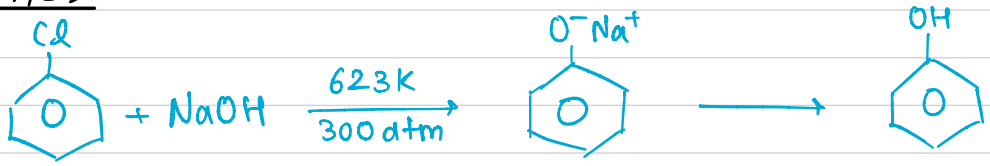
→ $HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$

→ $RCHO + R'MgX \longrightarrow R-\underset{R'}{CH}-OMgX \xrightarrow{H_2O} R-\underset{R'}{CH}-OH + Mg(OH)X$

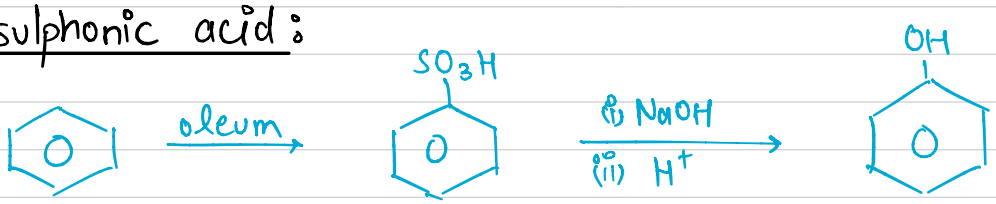
→ $RCOR + R'MgX \longrightarrow R-\underset{R}{\overset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R}{\overset{R'}{C}}-OH + Mg(OH)X$

Phenols

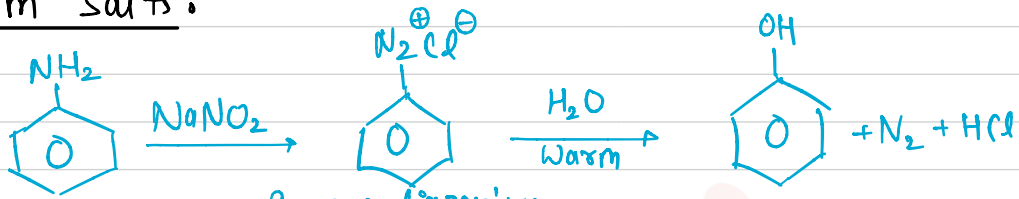
(1) From haloarenes:



(2) From benzene sulphonic acid:



(3) From diazonium salts:



Benzene diazonium chloride

(4) From Cumene:

↳ mentioned earlier

CHEMICAL REACTIONS

Note: Alcohols acts as both nucleophile and electrophile.

[I] Reactions involving cleavage of O-H Bond:

(i) Acidity of Alcohols and Phenols:

(a) Reaction with metals: Alcohols and Phenol react with active metal (Na, f, Al) to give Phenoxide

$$\Rightarrow \quad 2R\text{-}OH + 2Na \longrightarrow 2\text{-}R\text{-}O\text{-}Na + H_2$$

$$\Rightarrow \quad 6\,(H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OH) + 2Al \longrightarrow 2\,\left((H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}O)_3\right)Al + 3H_2$$

tert butyl alcohol — Aluminium tert-butoxide

$$\Rightarrow \quad \text{C}_6\text{H}_5\text{OH} + 2Na \longrightarrow 2\,\text{C}_6\text{H}_5\text{ONa} + H_2$$

(b) Acidity of alcohols:

$$\text{Acidity} \propto \frac{1}{\text{no. of attach group } (e^- \text{ releasing})}$$

$$R\text{-}CH_2OH \; > \; \underset{R}{\overset{R}{>}}CHOH \; > \; R\text{-}\underset{R}{\overset{R}{C}}\text{-}OH$$

1° 2° 3°

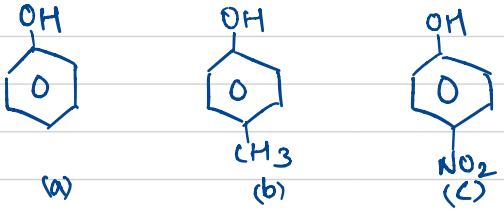
(c) Acidity of Phenols: Phenols react with aq. sodium hydroxide to form sodium Phenoxide but alcohols dont.

$$R\text{-}OH + NaOH \longrightarrow \text{No rx}^n$$

$$Ph\text{-}OH + NaOH \longrightarrow Ph\text{-}ONa + H_2O$$

i.e. acidity: $\boxed{Ph\text{-}OH > H_2O > R\text{-}OH}$

eg:



(a) (b) (c)

Acidity: c > a > b

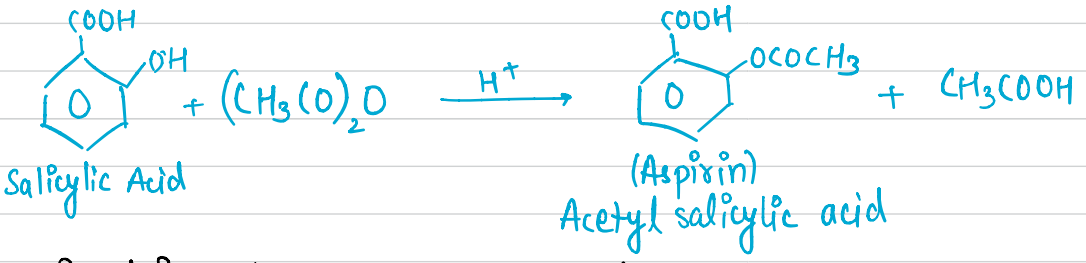
(ii) Esterification:

Alcohols and Phenols react with Carboxylic acid (COOH), Acid anhydride $(R'CO)_2O$ and acid chlorides $(R'COCl)$ to give Ester.

$Ar/ROH + R'COOH \xrightleftharpoons{H^+} Ar/ROCOR' + H_2O$

$Ar/ROH + (R'(O)_2O \xrightleftharpoons{H^+} Ar/ROCOR' + R'COOH$

$R/ArOH + R'COCl \xrightarrow[\text{pyrimidine}]{} R/ArOCOR' + HCl$



Salicylic Acid

(Aspirin)
Acetyl salicylic acid

[2] Reactions involving cleavage of C-O bond:

Reactions of cleavage of C-O bond only in Alcohols.
Phenols show this only with zinc.

(i) Reaction with hydrogen halides:

$$R-OH + HX \longrightarrow RX + H_2O$$

Alcohols soluble in lucas reagent, their halides are immiscible and produce turbidity.

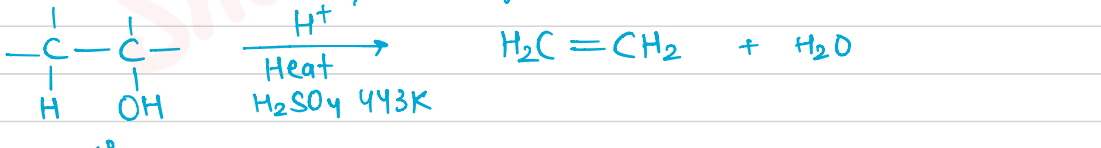
Tertiary alcohols → immidiate turbidity
Primary alcohols → no turbidity at room temperature

(ii) Reaction with Phosphorus trihalides:

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

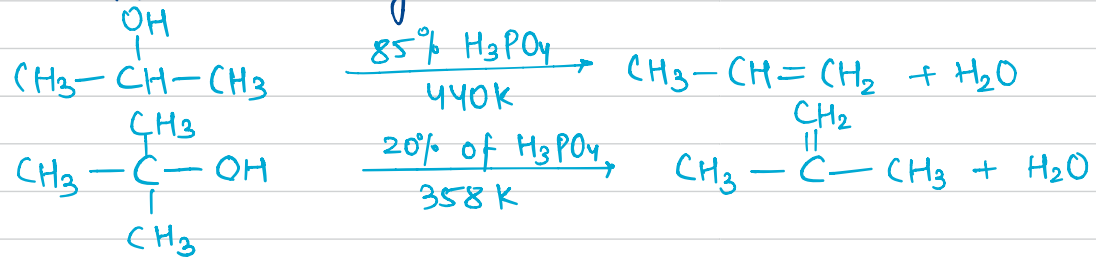
(X= Cl, Br)

(iii) Dehydration



1°

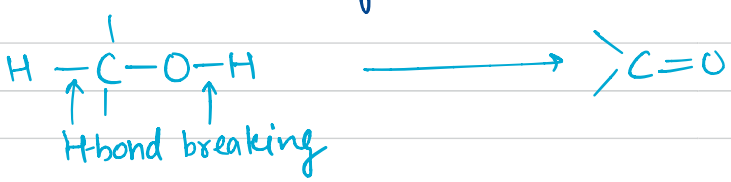
2° and 3° alcohols are dehydrated under milder condition:



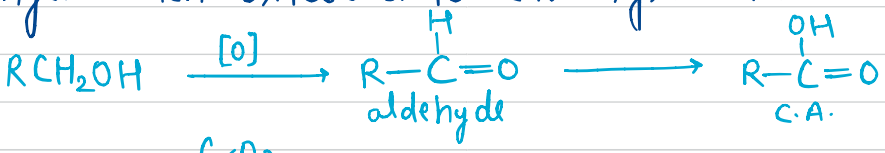
for dehydⁿ : 3° > 2° > 1°

(iv) Oxidation (dehydrogenation):

It means formation of carbon oxygen double bond with clevage of an O-H and C-H bonds.

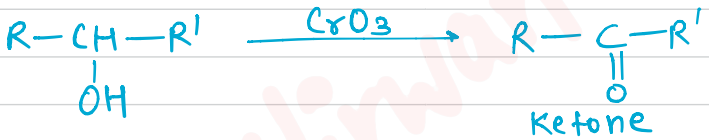


Note:
- loss of dihydrogen from alcohol molecule.
- Depend on oxi-agent used. 1° alcohol oxidise to aldehyde then oxidised to carboxylic acid.

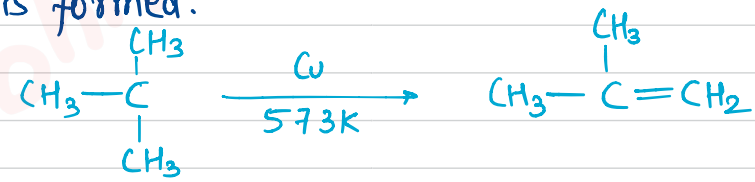


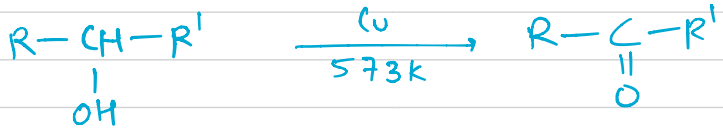
- strong oxi agent like acidified potassium permaganate
- Reagent for oxidation of **1° alco to aldehyde** in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyride and HCl.

- 2° alcohol ⟶ ketones



- 3° alcohol do not do oxd" but vapours of 1° and 2° passed over heated Cu at 573K, It takes place and aldehyde or ketone is formed.

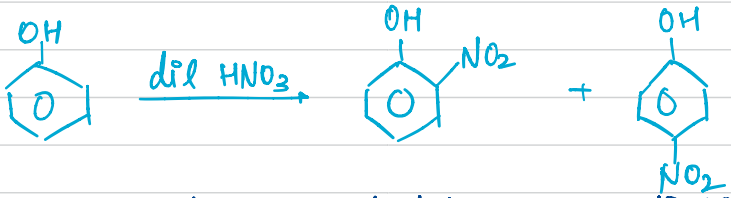




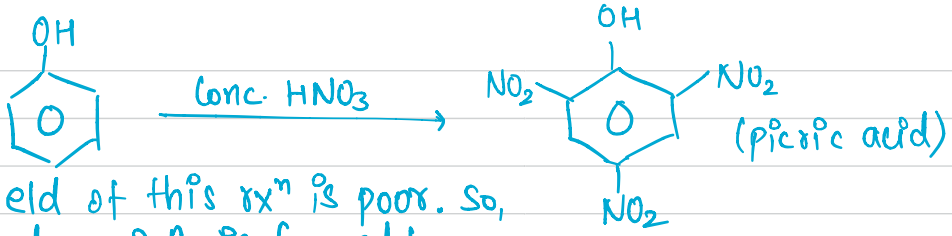
[3] Reactions of Phenols only:

(i) Electrophilic aromatic substitution:

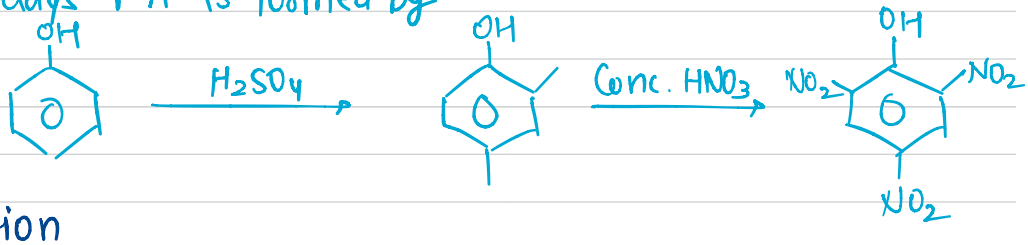
(a) Nitration



Imp: O and P isomers can be separated by steam distillation, O-Nitrophenol is steam volatile due to Intramolecular H-bonding. while P-Nitrophenol is less volatile due to Intermolecular H-bonding.

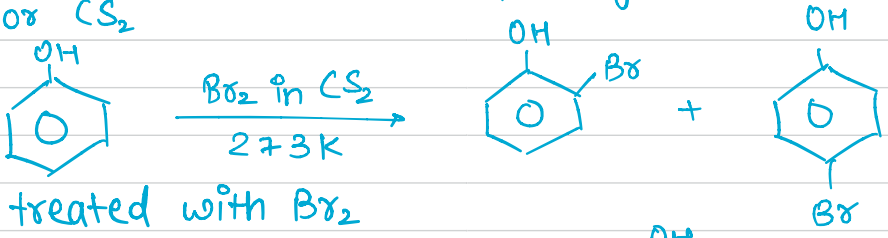


↳ but yield of this rxn is poor. So,
Now a days P.A. is formed by

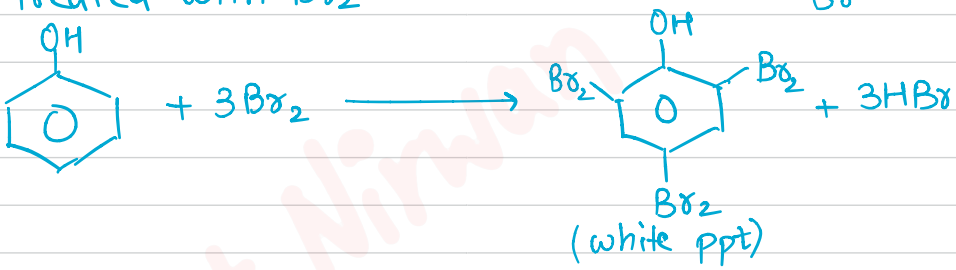


(b) Halogenation

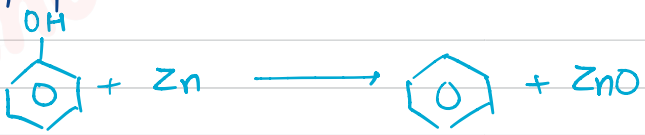
→ Reaction is carried out in low polarity solvents like $CHCl_3$ or CS_2



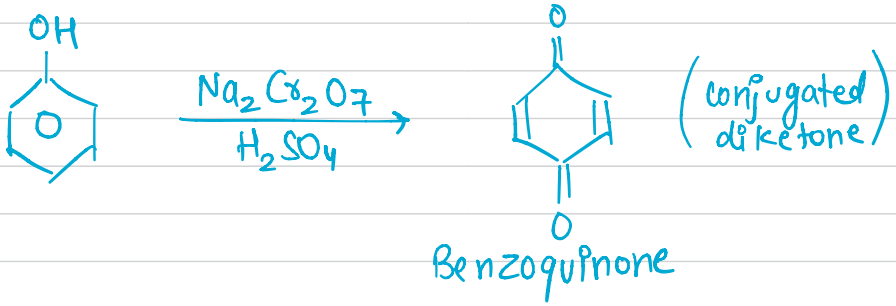
→ Phenol treated with Br_2



(c) Kolbe's reaction
(d) Reimer-Tieman Reaction
(e) Reaction of phenol with Zn dust



(f) Oxidation



Ethers

PREPARATION:

(1) By dehydration of alcohols

CH_3-CH_2OH —(H_2SO_4, 443 K)→ $CH_2=CH_2$

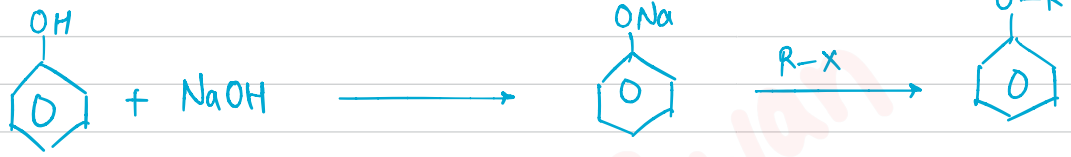
CH_3-CH_2OH —(H_2SO_4, 413 K)→ $C_2H_5OC_2H_5$

(2) Williamson Synthesis:

Only for 1° alkyl halide, if 3° is used then alkene is formed.

$$R-X + R'-ONa \longrightarrow R-O-R' + NaX$$

Phenols also converted

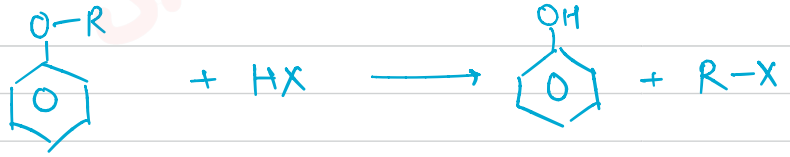


CHEMICAL REACTIONS:

(1) Cleavage of C-O bond in ethers:

$$R-O-R + HX \longrightarrow RX + R-OH$$

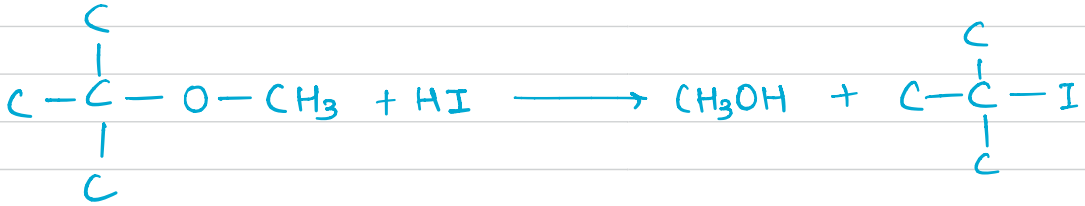
$$R-OH + HX \longrightarrow R-X + H_2O$$



$$R-OR' + HX \longrightarrow R-X + R'-OH$$

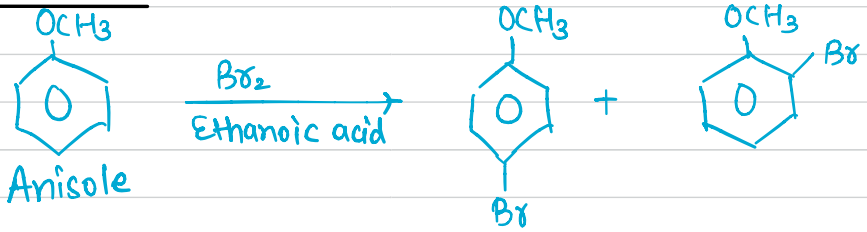
HI > HBr > HCl reactivity of hydrogen halide

for 3°:

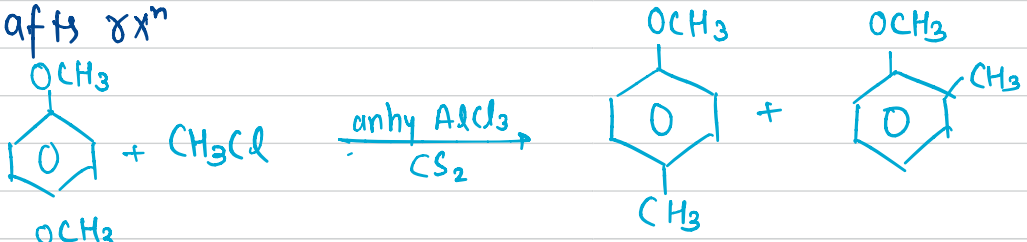


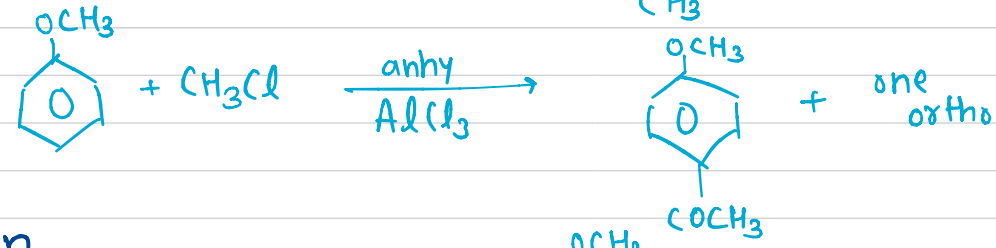
(2) Electrophilic Substitution:

→ Halogenation:



→ Friedel - Crafts rxn





→ Nitration