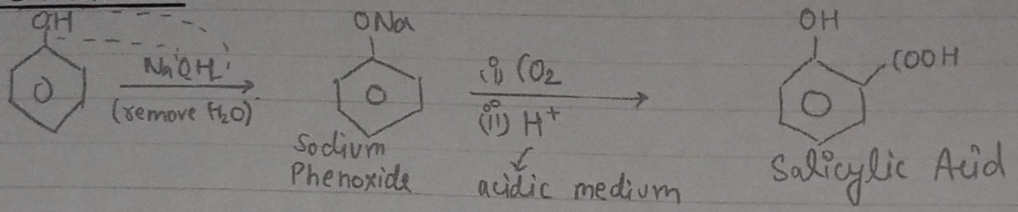
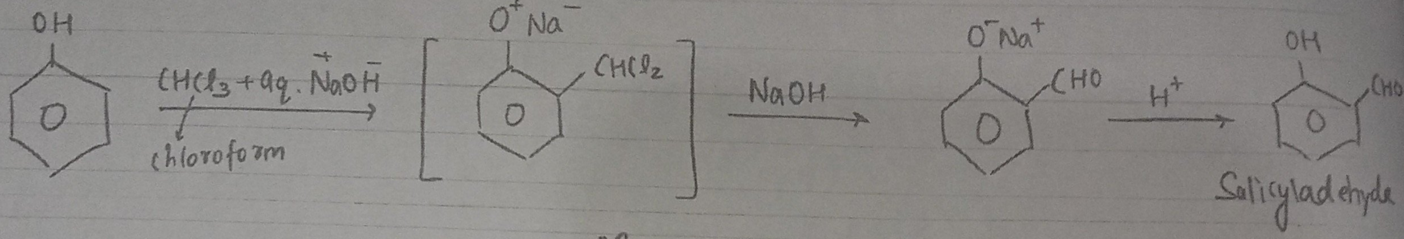
NAME REACTIONS OF THIS CHAPTER

(1) Kolbe's Reaction:



(2) Reimer - Tiemann Reaction:



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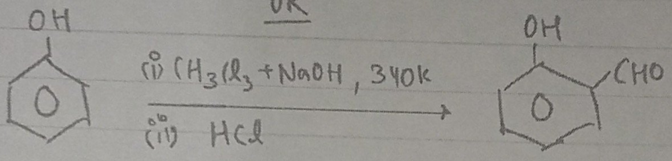


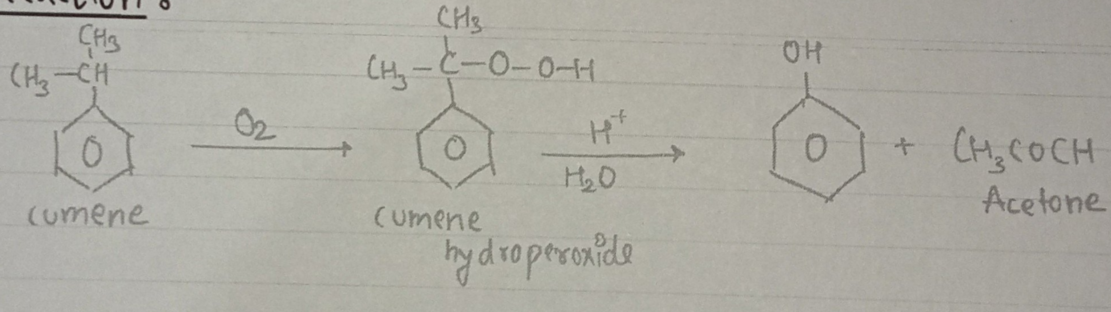
(3) Williamson Synthesis:

$$\overset{-\ \oplus}{R-ONa} + \overset{\delta^+\ \ \delta^-}{R-X} \xrightarrow[-NuX]{SN^2} ROR + NaX$$

Sodium alkoxide   Alkyl halide   ether

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

(4) Cumene Reaction:

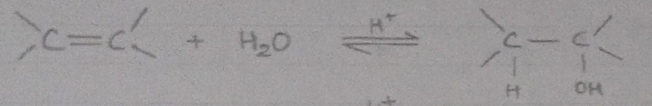


PREPARATIONS

Alcohols

1) from Alkene:

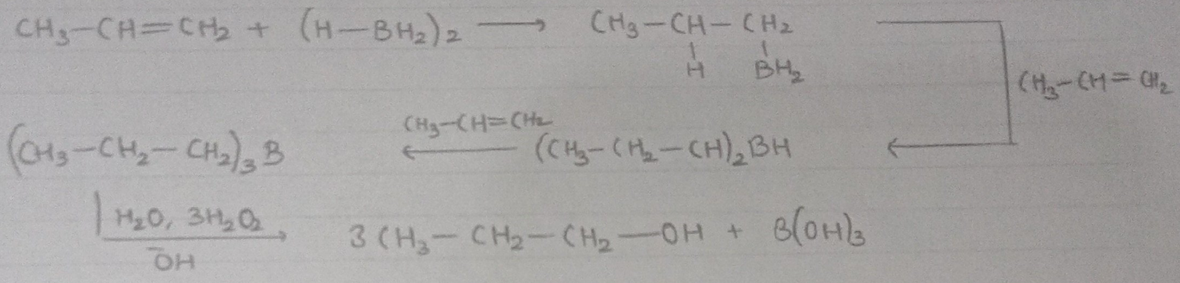
→ By Acid Catalysted hydration:



$$>C=C< + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} >\underset{H}{C}-\underset{OH}{C}<$$

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

→ By hydrocarboration oxydation:



$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2}$$

$$\xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH)_2BH \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_3B$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow[\bar{O}H]{H_2O,\ 3H_2O_2} 3(CH_3-CH_2-CH_2-OH + B(OH)_3$$

2) from Carbonyl Compounds:

→ By reduction of Aldehydes and ketones:

Add^n 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

$$RCHO + H_2 \xrightarrow{Pd} R-CH_2-OH$$

$$RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

K^3B: 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:

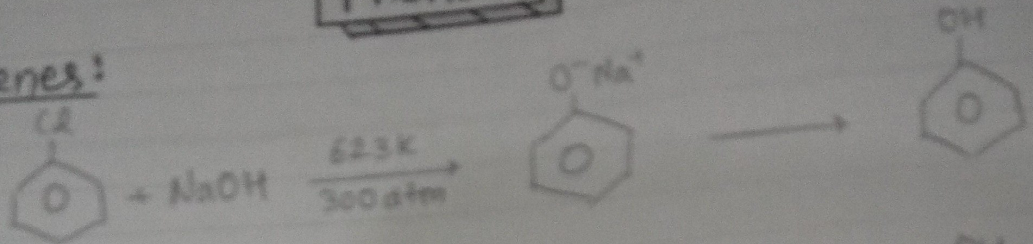
→ $HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$

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

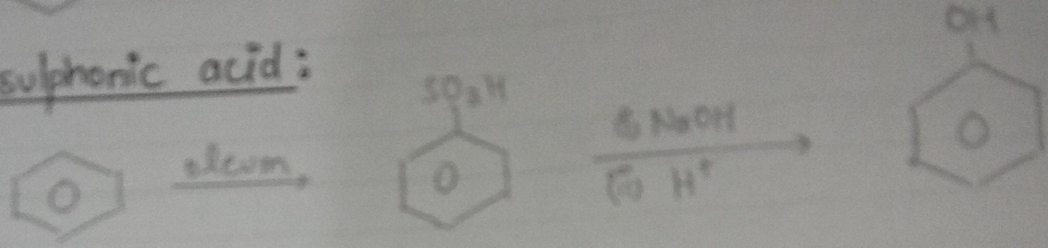
→ $RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$

Phenols

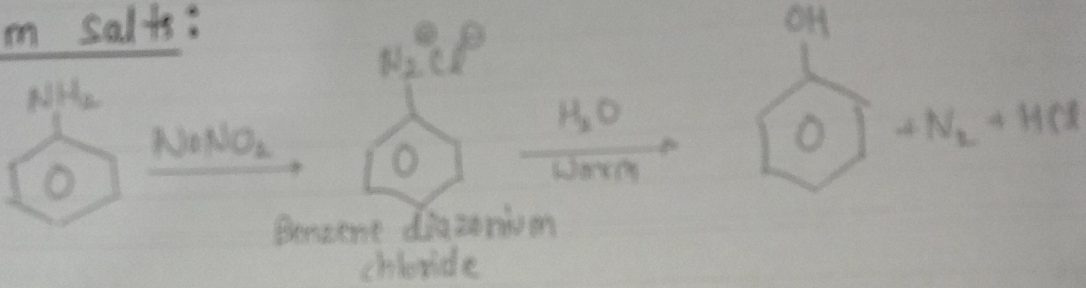
(1) From haloarenes:



(2) From benzene sulphonic acid:



(3) From diazonium salts:



(4) From Cumene:

↳ mentioned earlier

CHEMICAL REACTIONS

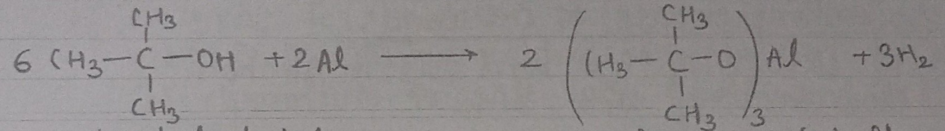
Note: Alcohols acts as both nucleophile and electrophile.

1] Reactions involving clevage of O-H Bond:

(i) Acidity of Alcohols and Phenols:

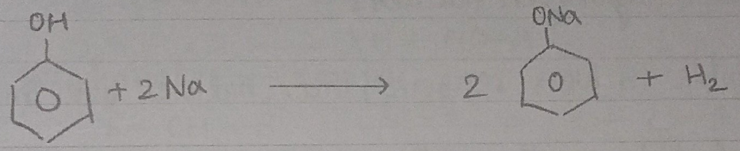
(a) Reaction with metals: Alcohols and Phenol react with active metal (Na, f, Al) to give Phenoxide

⇒ $2R{-}OH + 2Na \longrightarrow 2{-}R{-}O{-}Na + H_2$

⇒ 

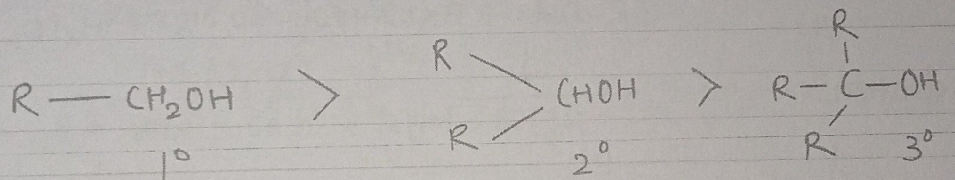
$$6\,CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH + 2Al \longrightarrow 2\left(CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O\right)_3 Al + 3H_2$$

tert butyl alcohol — Aluminium tert-butoxide

⇒ 

(b) Acidity of alcohols:

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



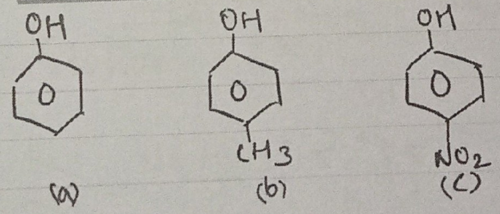
$$\underset{1^\circ}{R{-}CH_2OH} > \underset{2^\circ}{R_2CHOH} > \underset{3^\circ}{R{-}\overset{R}{\underset{R}{C}}{-}OH}$$

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

$R{-}OH + NaOH \longrightarrow$ No rxn

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

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

eg: 

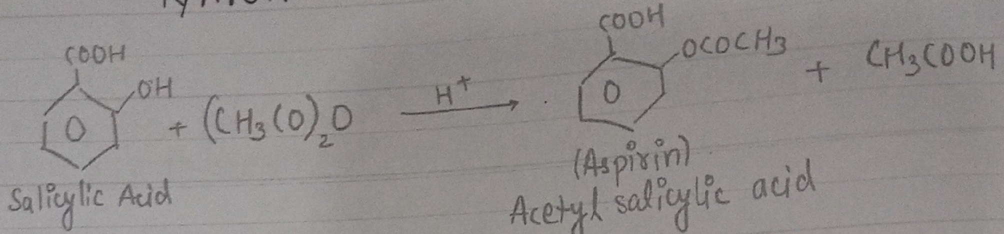
Acidity: c > a > b

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

$$Ar/ROH + R'COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$$

$$Ar/ROH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyrimidine}} R/ArOCOR' + HCl$$



Salicylic Acid

(Aspirin)
Acetyl salicylic acid

(2) Reactions involving clevage of C-O bond:

Reactions of clevage 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.

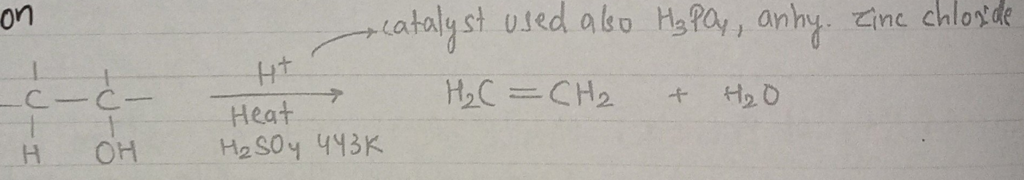
Tertiary alcohols → immidiate turbidity
Primary alcohols → no turbidity at room temperature

(ii) Reaction with Phosphorus trihalides:

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

$(X = Cl, Br)$

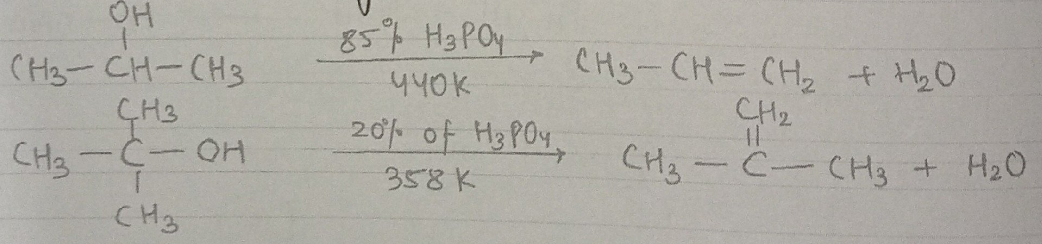
(iii) Dehydration



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\substack{\text{Heat}\\ H_2SO_4\ 443K}]{H^+} H_2C=CH_2 + H_2O$$

1°

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

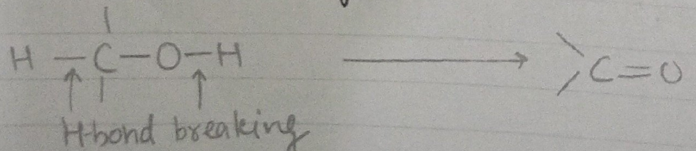


$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[440K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[358K]{20\%\ \text{of}\ H_3PO_4} CH_3-\overset{CH_2}{\overset{||}{C}}-CH_3 + H_2O$$

for dehyd^n : 3° > 2° > 1°

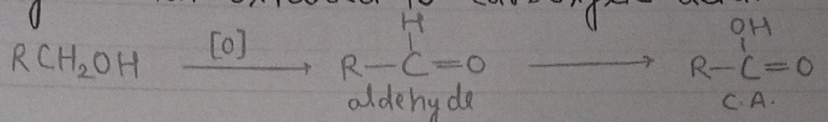
(iv) Oxidation (dehydrogenation): It means formation of carbon oxygen double bond with clevage of an O-H and C-H bonds.



$$H-\overset{|}{C}-O-H \longrightarrow \;>C=O$$

Note:

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



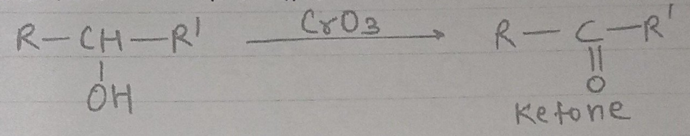
$RCH_2OH \xrightarrow{[O]} \underset{\text{aldehyde}}{R-\overset{H}{C}=O} \longrightarrow \underset{\text{C.A.}}{R-\overset{OH}{C}=O}$

$RCH_2OH \xrightarrow{CrO_3} RCHO$

- 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.

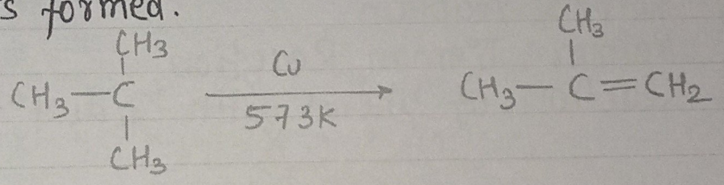
$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$

- 2° alcohol ⟶ ketones



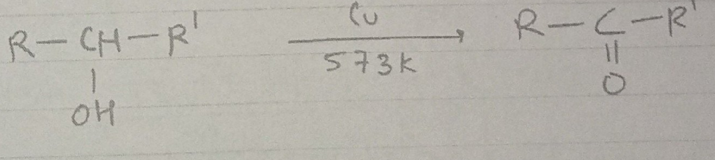
$R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{O}{\overset{\|}{C}}-R'}$

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



$CH_3-\overset{CH_3}{\underset{CH_3}{C}} \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{C}=CH_2$

$RCH_2OH \xrightarrow[573K]{Cu} RCHO$

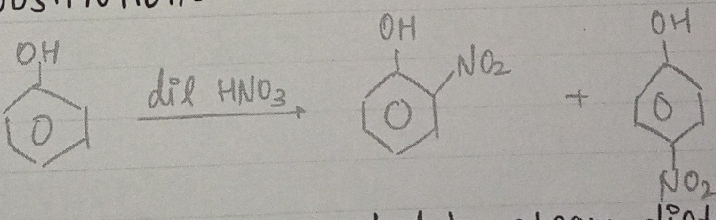


$R-\underset{OH}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{O}{\overset{\|}{C}}-R'$

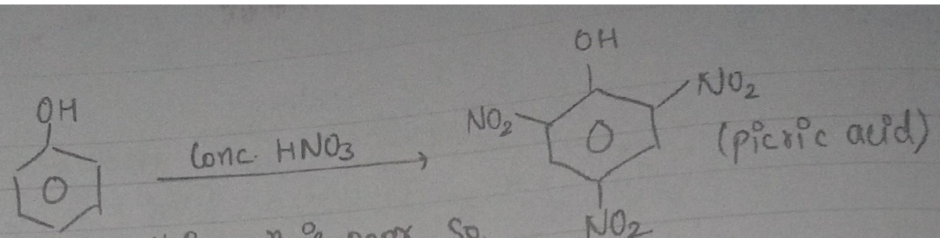
) Reactions of Phenols only:

(i) Electrophilic aromatic substitution:

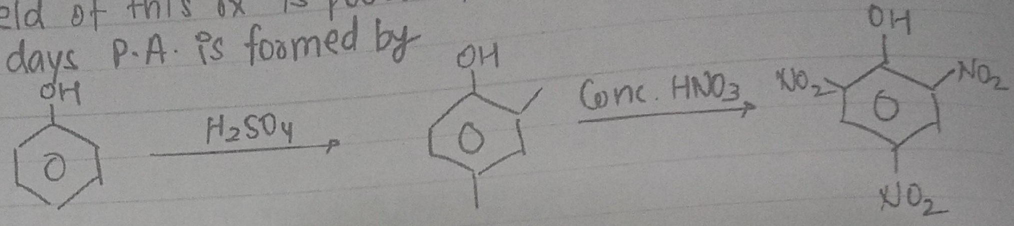
(a) Nitration



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.

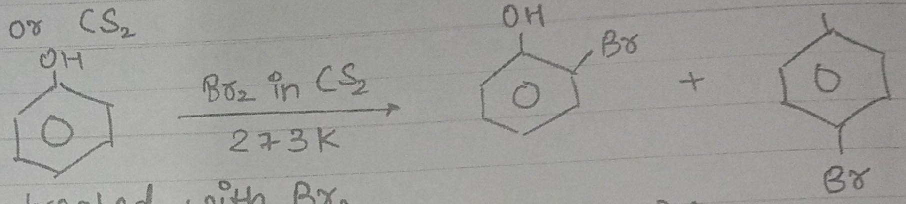


↳ but yield of this rx^n is poor. So,
Now a days P.A. is formed by

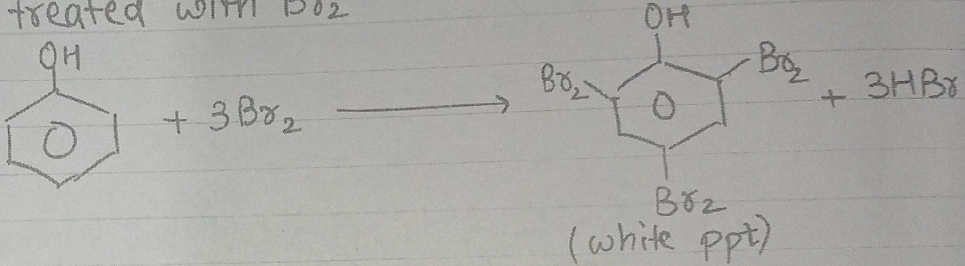


(b) Halogenation

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



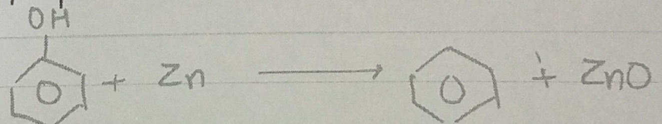
→ Phenol treated with Br_2



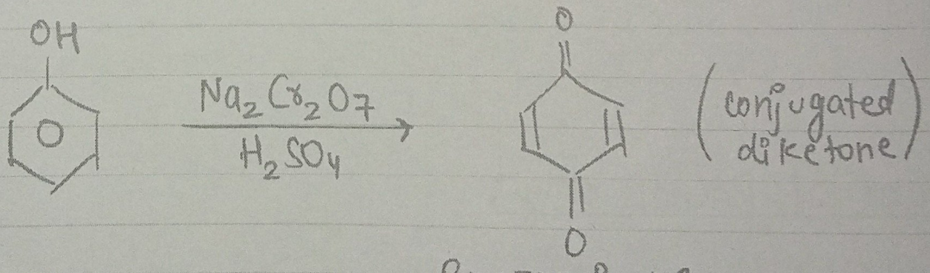
(c) Kolbe's reaction

(d) Reimer-Tieman Reaction

(e) Reaction of phenol with Zn dust



(f) Oxidation



Benzoquinone

Ethers

PREPARATION:

(1) By dehydration of alcohols

$$CH_3-CH_2OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2$$

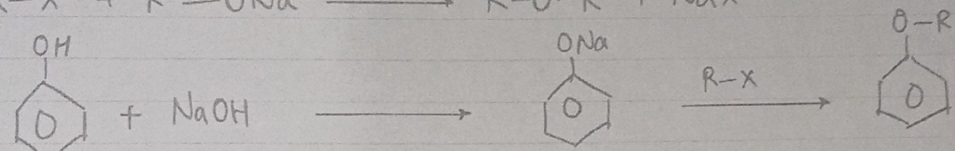
$$CH_3-CH_2OH \xrightarrow[413K]{H_2SO_4} C_2H_5OC_2H_5$$

(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

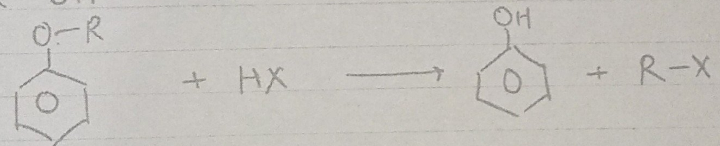


CHEMICAL REACTIONS:

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

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

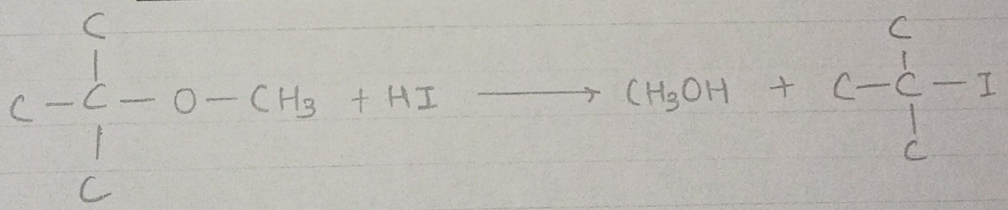
$$R-OH + HX \longrightarrow R-X + H_2O$$



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

$\boxed{HI > HBr > HCl}$ reactivity of hydrogen halide

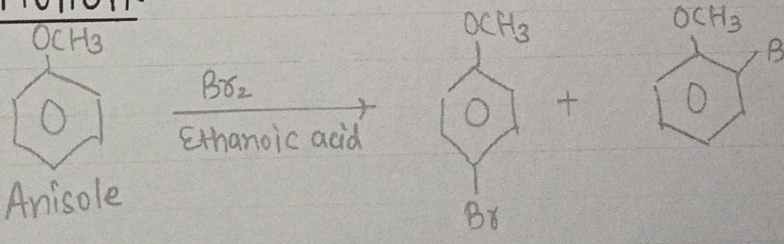
for 3°:



$$C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-I$$

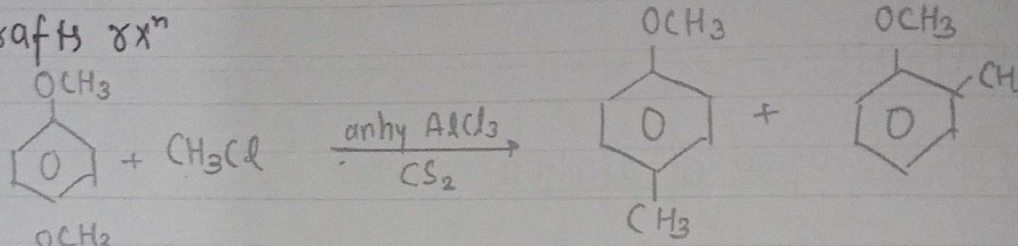
(2) Electrophilic Substitution:

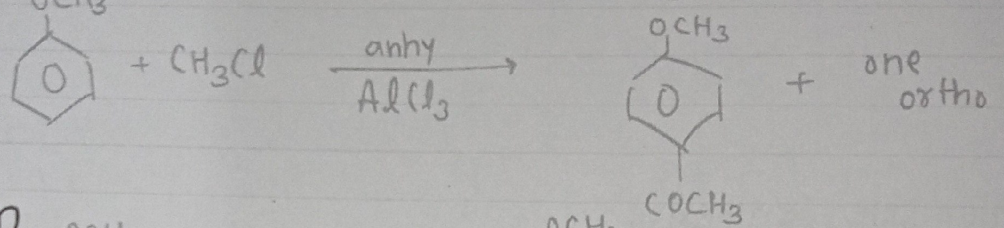
→ Halogenation:



Anisole

→ Friedel - Crafts rx^n





→ Nitration