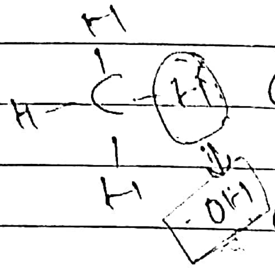
Unit - 11

Alkohols, phenol, and Ethers.

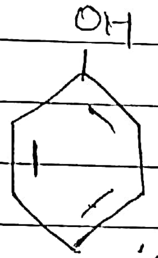
(0) Introduction.



CH_4 – Methane [Hydrocarbon]

CH_3OH → Methanol [Alcohol]

↳ Hydroxy group.

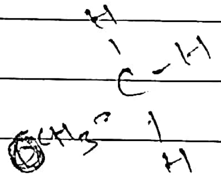


→ phenol.

C_6H_6

C_6H_5OH → phenol

C_6H_5OH.



CH_3OCH_3 – dimethyl ether.

↳ Alkoxy group

Classification:

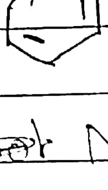
[a] Alcohol and phenols

→ They are Classified as, Mono, Di, Tri or polyhydric

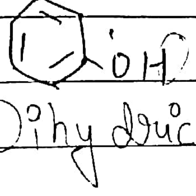
Ex: CH_2H_5OH

CH_2-OH
CH_2-OH

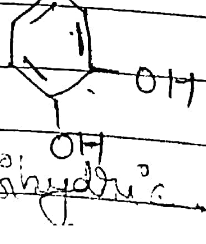
$CHOH$
$CHOH$
$CHOH$



~~Moot~~ Monohydric



Dihydric



Trihydric

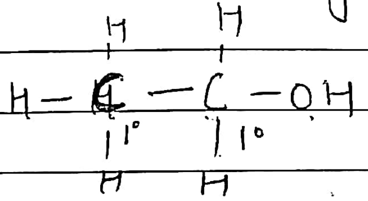
→ Monohydric alcohol further classified to hybridisation of Carbon atom to which hydroxy group is attached.

(i) Compound Containing $C_{sp^3}-OH$ bond.

→ $-OH$ group is attached to sp^3 hybridised Carbon.

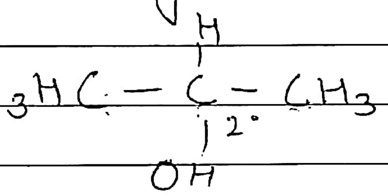
→ They are further classified as.

[a] Primary, Secondary and Tertiary ~~alt~~ alcohol.



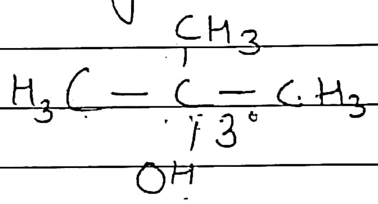
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|\,1^\circ}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|\,1^\circ}{C}}}}-OH$$

primary (1°)



$$_3HC-\overset{H}{\underset{OH}{\overset{|}{\underset{|\,2^\circ}{C}}}}-CH_3$$

Secondary (2°)



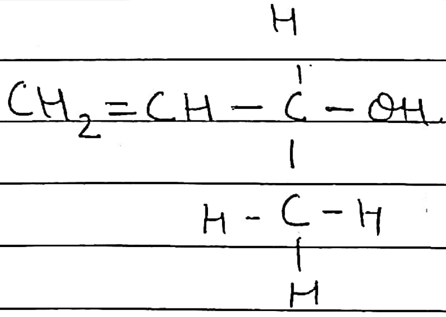
$$H_3C-\overset{CH_3}{\underset{OH}{\overset{|}{\underset{|\,3^\circ}{C}}}}-CH_3$$

Tertiary (3°)

[b] Allylic alcohol.

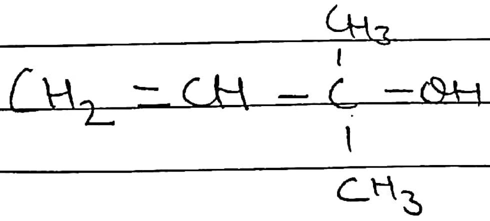
$CH_2=CH-CH_2-OH$

primary



$$CH_2=CH-\overset{H}{\underset{\underset{H}{\overset{|}{H-C-H}}}{\overset{|}{\underset{|}{C}}}}-OH$$

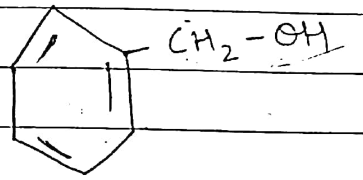
Secondary



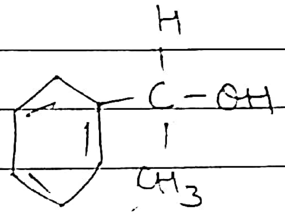
$$CH_2=CH-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

Tertiary.

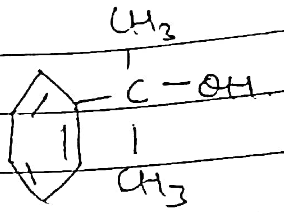
[C] Benzylic alcohol.



1°



2°



3°

[ii] Compound Containing $C_{sp^2}-OH$ bond:

$CH_2=CH-OH$ (Vinyllic alcohol)

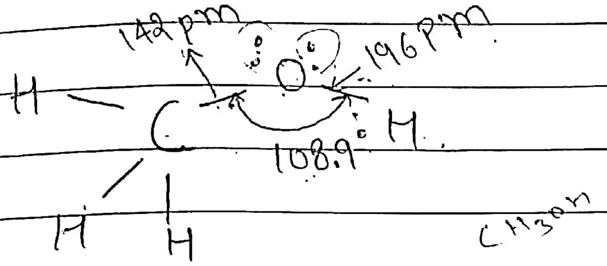
[B] Ethers

→ They are Classified as Simple/Symmetrical and Mixed/Unsymmetrical.

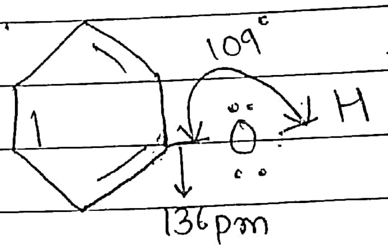
For ex: (i) $C_2H_5OC_2H_5$ → Symmetrical ether

(ii) $C_2H_5-OCH_3$ → Unsymmetrical.

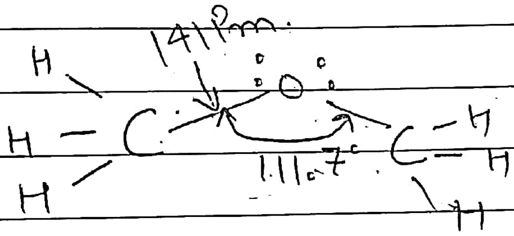
Structure of functional group.



Methanol.



phenol.



→ Methoxy methane. (ether)

Q. The bond angle in alcohol is slightly less than tetrahedral angle (109°-28'). why ?

Ans Due to the repulsion b/w the unshared pairs of electron of oxygen.

Q. Carbon - oxygen bond length in phenol is less than that in methanal. why ?

Ans (i) due to partial double bond character

(ii) Sp^2 hybridised State of Carbon to which oxygen is attached. [50% S-character]

Q. The bond angle in Methoxymethane [ether] is slightly greater than tetrahedral angle. why ?

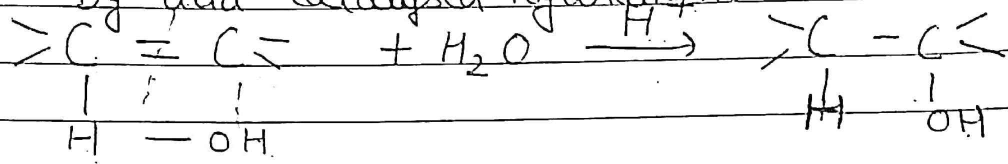
Ans due to bulky alkyl groups.

Alcohols and phenols.

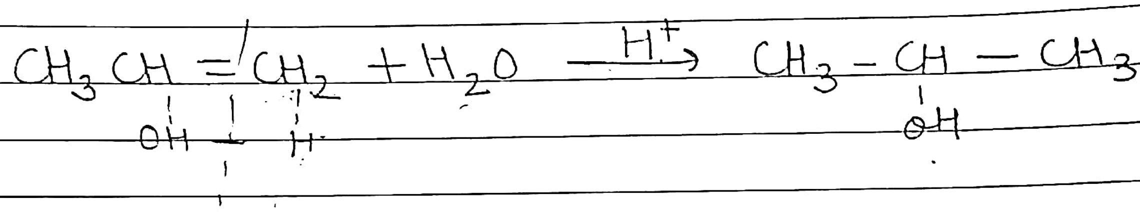
⊙ Preparation of Alcohols.

1. from alkenes

(i) By acid Catalysed hydration.

⊙ 

$>C=C< + H_2O \xrightarrow{H} >C-C<$

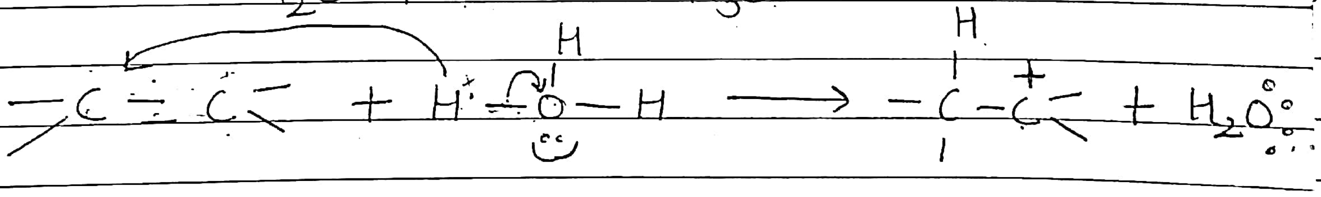
⊙ 

$CH_3CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-CH(OH)-CH_3$

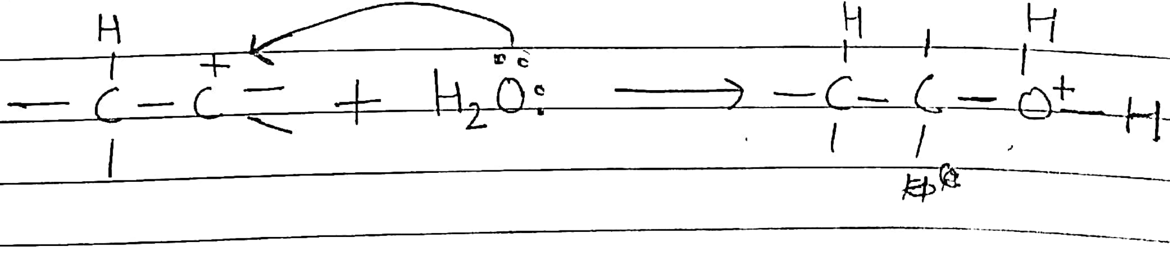
→ Mechanism

STEP-1 Protonation of alkene to form Carbocation be electrophillic attack of H_3O^+.

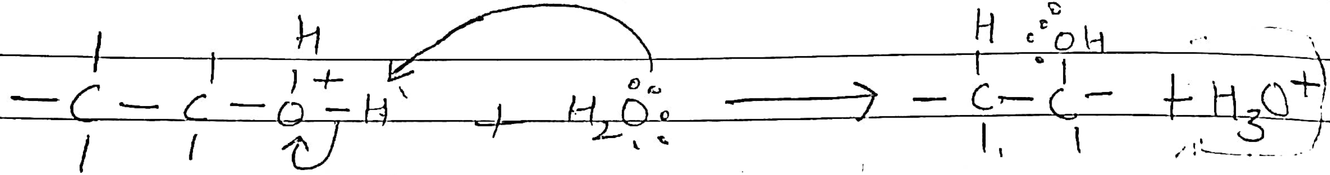
$$H_2O + H^+ \longrightarrow H_3O^+$$



STEP-2: Nucleophillic attack of water on Carbocation.



STEP-3 Deprotonation to form an alcohol.



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{H}{\overset{|+}{\ddot{O}}}-H + H_2\ddot{O}: \longrightarrow -\overset{H}{\underset{|}{C}}-\overset{\ddot{O}H}{\underset{|}{C}}- + H_3O^+$$

(ii) From ~~Os~~ By hydroboration Oxidation.

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

$$\downarrow CH_2-CH=CH_2$$

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

$$H_2O \quad \downarrow 3H_2O_2,\ \overset{\ominus}{O}H$$

$$3\,CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propane-1-ol.

$$3CH_3-CH=CH_2 \xrightarrow[H_2O_2,\ OH^-]{B_2H_6} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

2. from Carbonyl Compounds.

[i] Reduction of aldehyde and ketone.

⊙ $RCHO + H_2 \xrightarrow{Pd} RCH_2OH$

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

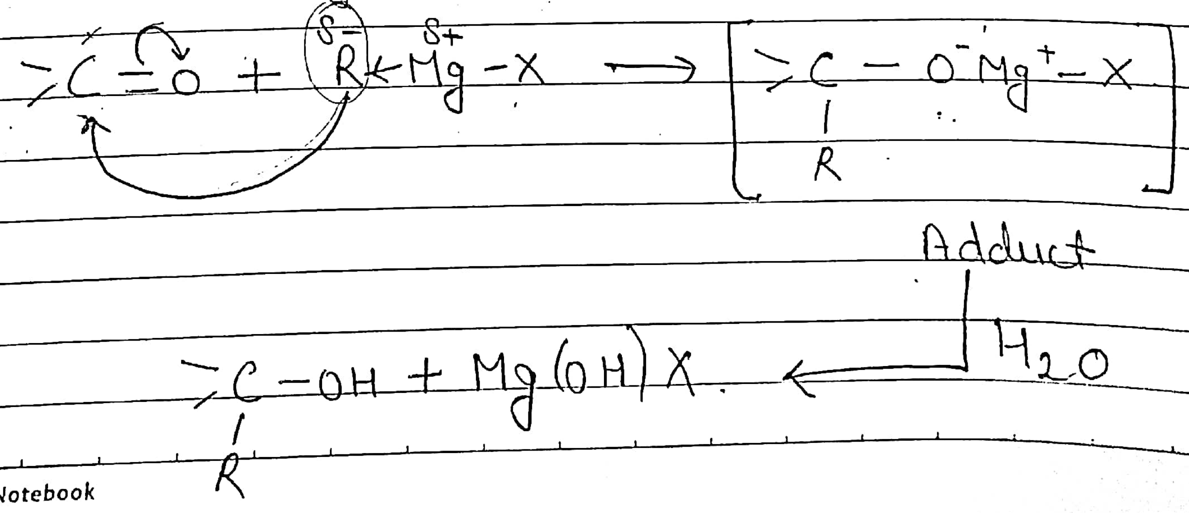
NOTE Aldehyde → primary alcohols
Ketone → Secondary alcohols

[ii] By reduction of Carboxylic acid and ester.

⊙ $RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH.$ (expansive)

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

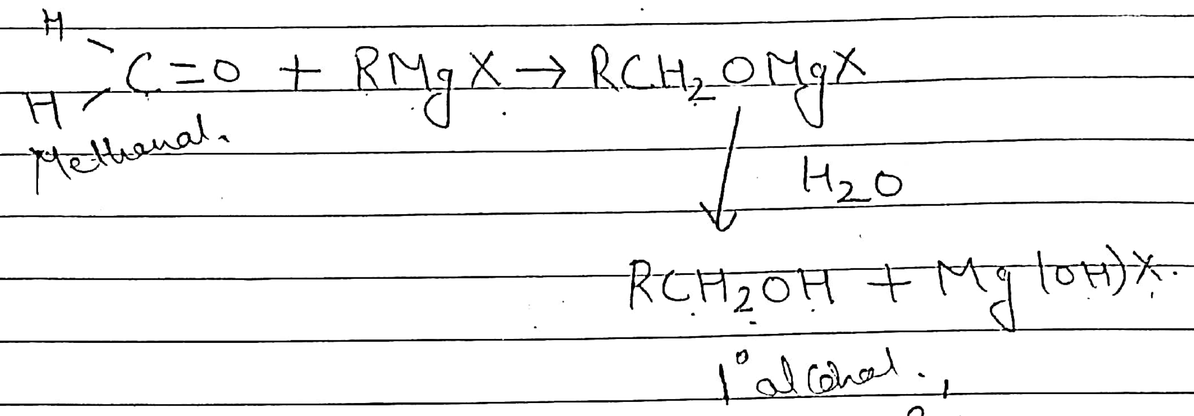
3. From Grignard reagent.



$$>C=O + \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X \longrightarrow \left[>\underset{\displaystyle R}{\underset{|}{C}}-O^-Mg^+-X\right]$$

Adduct

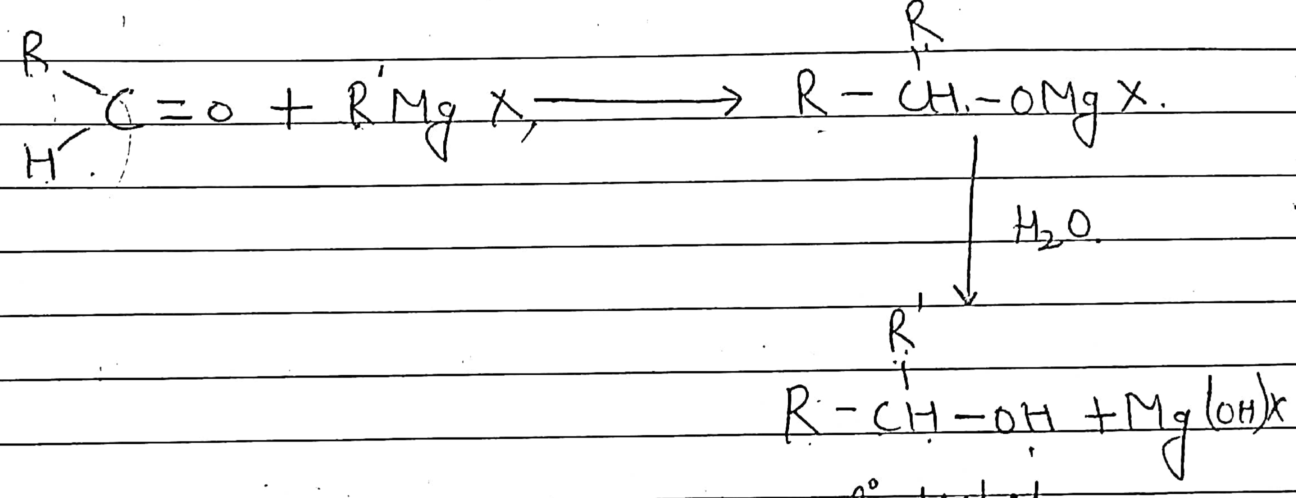
$$\left[>\underset{\displaystyle R}{\underset{|}{C}}-O^-Mg^+-X\right] \xrightarrow{H_2O} >\underset{\displaystyle R}{\underset{|}{C}}-OH + Mg(OH)X.$$

⊙ 

$$\genfrac{}{}{0pt}{}{H}{H}\!\!>C=O + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

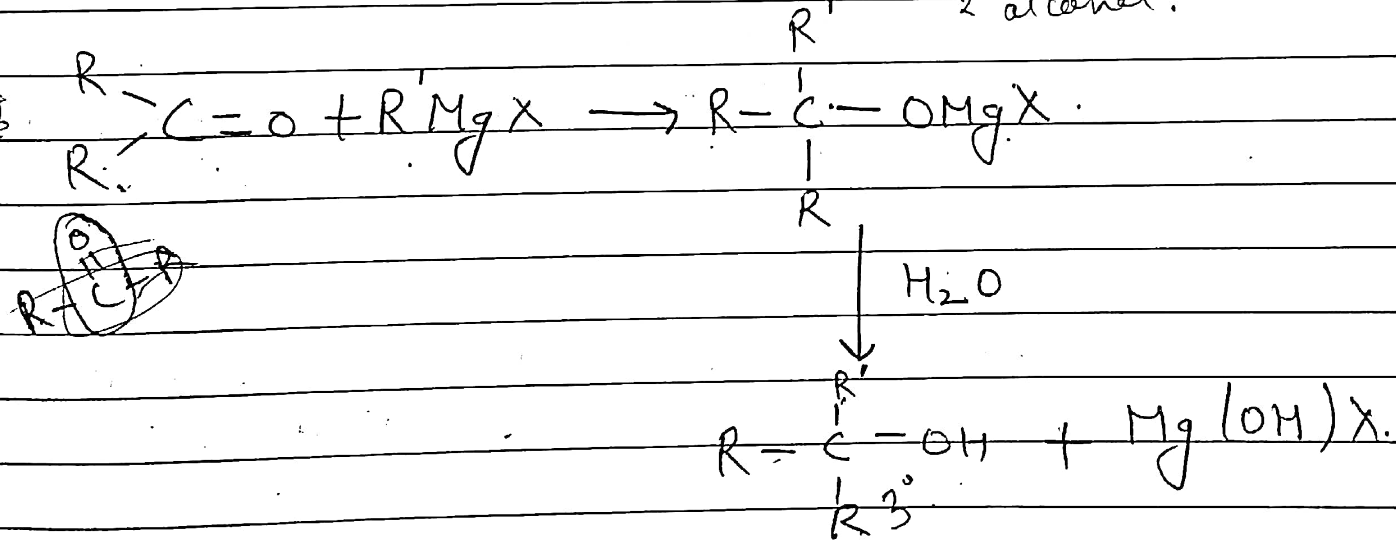
Methanal.

1° alcohol.

⊙ 

$$\genfrac{}{}{0pt}{}{R}{H}\!\!>C=O + R'MgX \rightarrow R-\overset{R'}{\overset{|}{C}}H-OMgX \xrightarrow{H_2O} R-\overset{R'}{\overset{|}{C}}H-OH + Mg(OH)X$$

2° alcohol.

⊙ 

$$\genfrac{}{}{0pt}{}{R}{R}\!\!>C=O + R'MgX \rightarrow R-\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}-OMgX \xrightarrow{H_2O} R-\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}-OH + Mg(OH)X$$

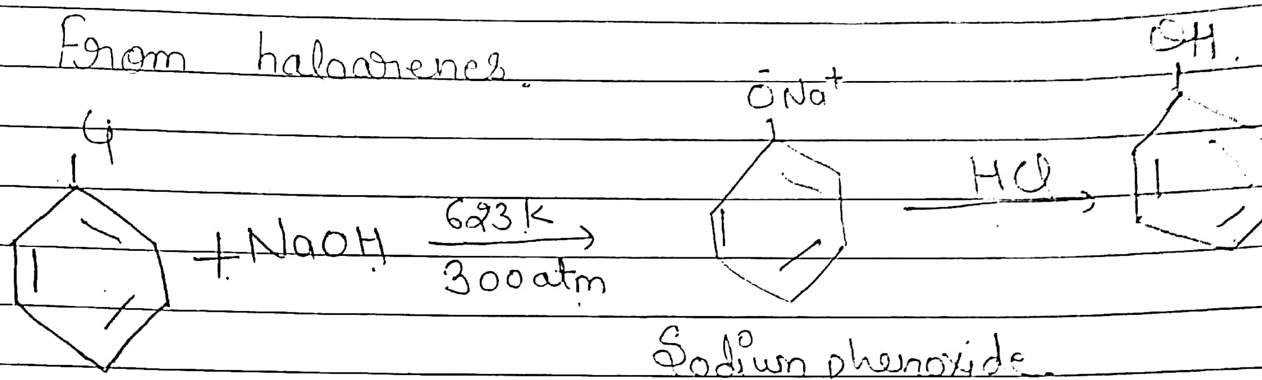
3°

NOTE

Methanal → primary alcohol.
aldehyde → Secondary alcohol.
Ketone → tertiary alcohol.

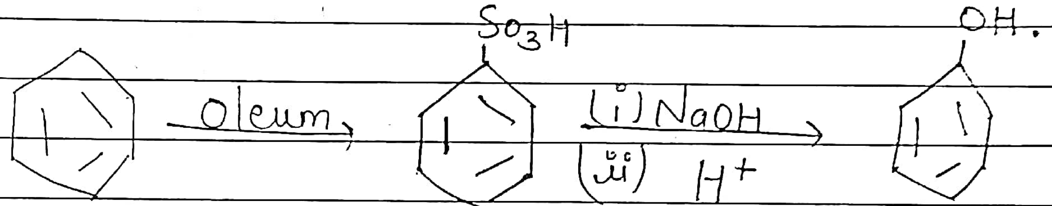
Preparation of phenol.

1 From haloarenes.



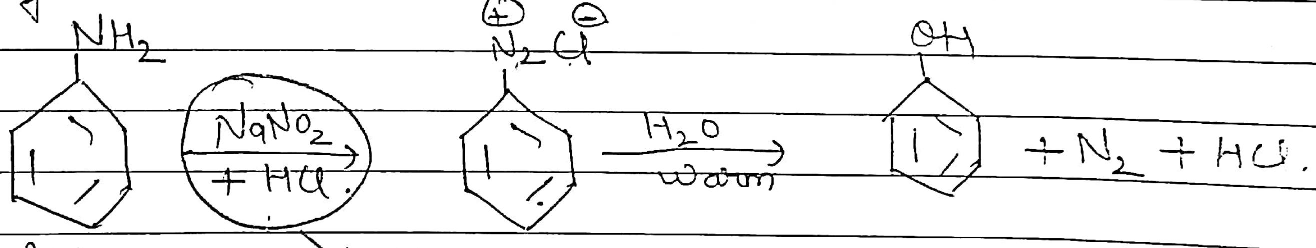
Sodium phenoxide.

2 from benzenesulphonic acid.



Benzene Solphonic acid.

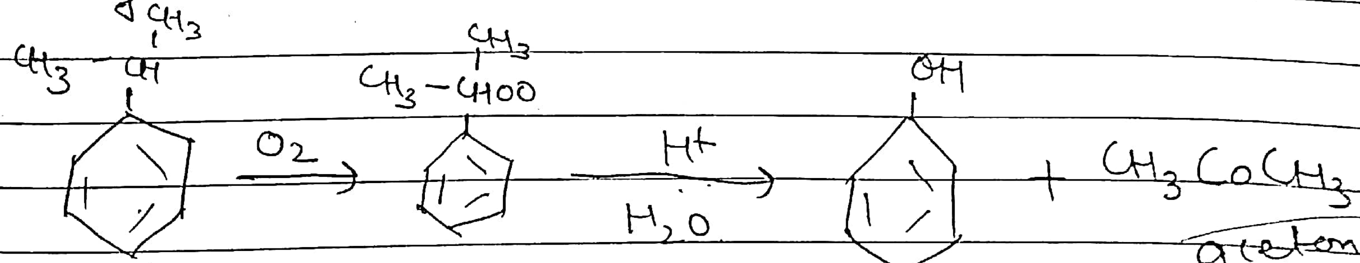
3. from diazonium Salt



Aniline

Nitrous acid

4. from Cumene.



acetone → large amount.

Cumene

Cumene hydroperoxide.

Phenol

Physical properties.

⊙ Boiling point.

→ B.P of alcohols and phenol increase with increase in number of carbon atoms.

→ B.P of alcohols decrease with increasing in branching. As Van der Waals force decrease with decrease is surface area.

Note :- B.P of alcohols and phenol higher in comparison to other class of compound (Hydrocarbon). due to the presence of intermolecular hydrogen bonding.

⊙ Solubility.

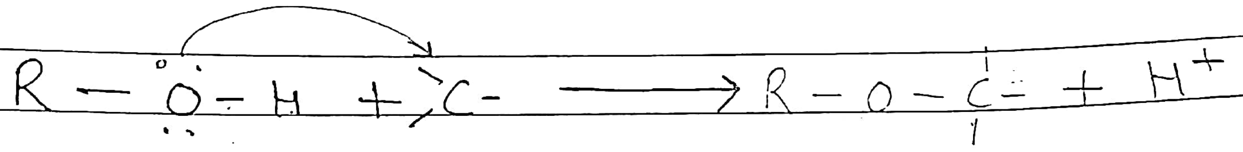
→ Solubility of alcohol and phenol ~~is~~ in water is due to their ability to form hydrogen bond with water.

→ Solubility decrese with increase in size of alkyl/aryl (hydrophobic) group.

CHEMICAL REACTIONS.

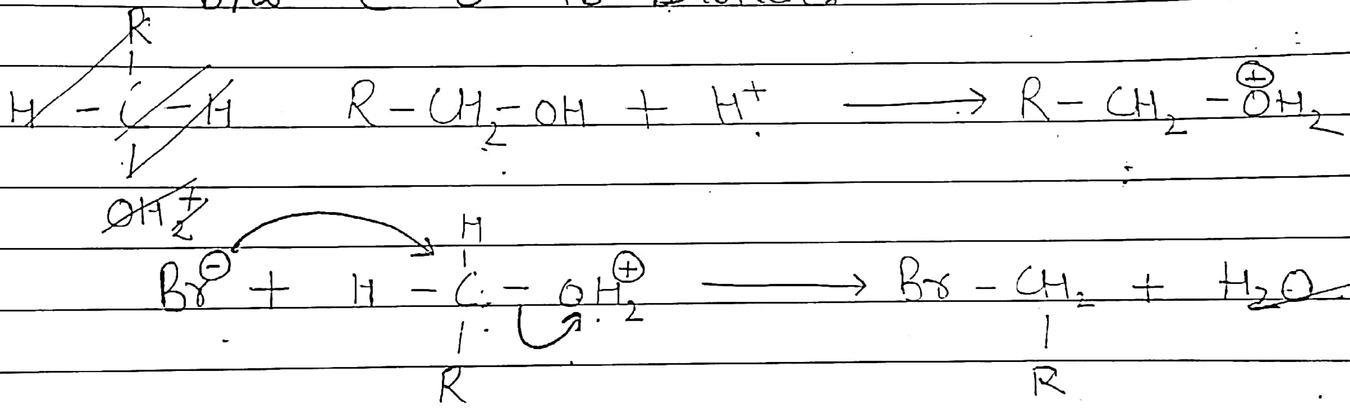
- Alcohols are versatile Compounds. They react as nucleophiles as well as electrophiles.

NOTE: when alcohol react ~~with~~ as nucleophiles bond b/w O–H is broken.



$R - \ddot{O} - H + \rangle C - \longrightarrow R - O - \overset{|}{\underset{|}{C}} - + H^+$

(ii) when alcoh react as electrophiles. bond b/w C–O is broken.



$R - CH_2 - OH + H^+ \longrightarrow R - CH_2 - \overset{\oplus}{O}H_2$

$Br^{\ominus} + H - \overset{H}{\underset{R}{C}} - \overset{\oplus}{O}H_2 \longrightarrow Br - \underset{R}{CH_2} + H_2O$

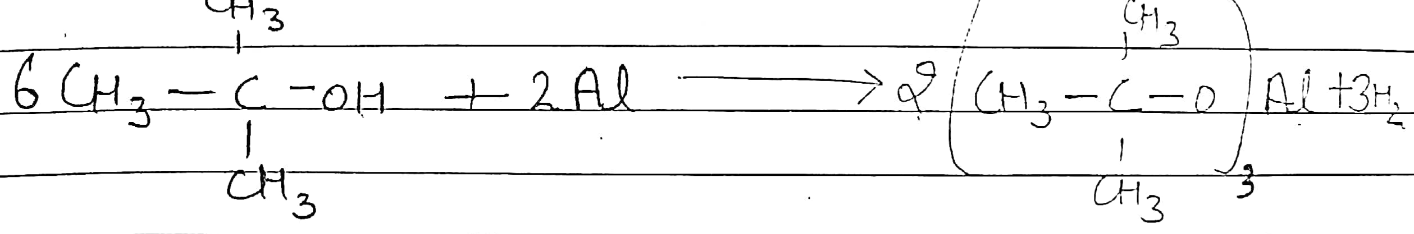
[a] Reaction involving Cleavage of O–H bond.

1. Acidity of alcohols and phenols.

→ Alcohol and phenol react with Metal Such as Sodium, potassium and aluminium to yield alkoxide/phenoxide.

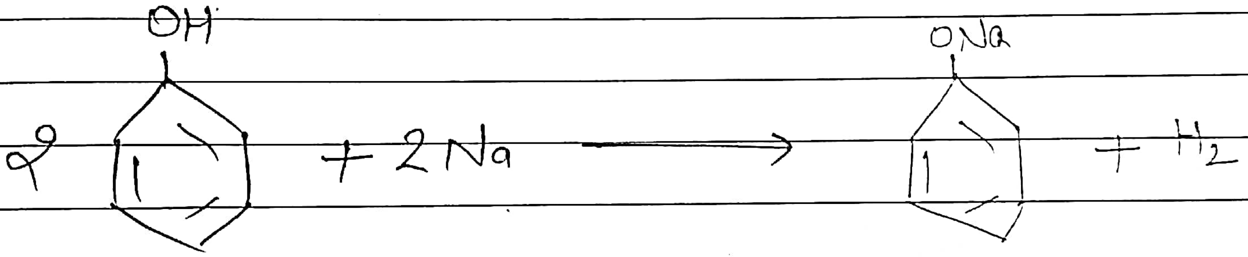
⊙ $2R-O-H + 2Na \longrightarrow 2R-O-Na + H_2$

Sodium alkoxide.

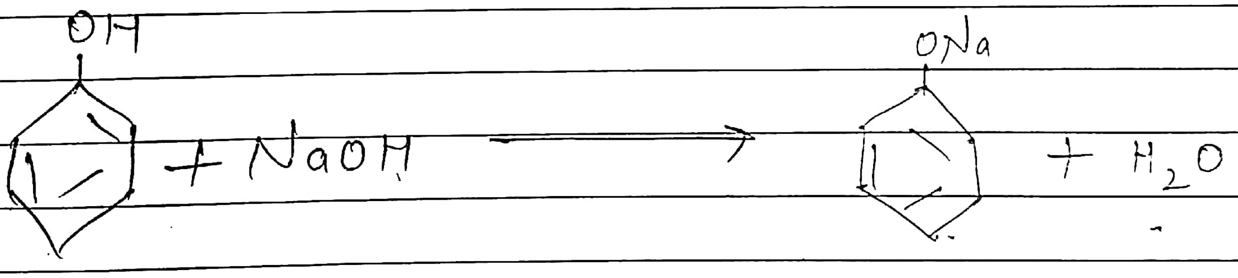
⊙ 

$6\,CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + 2Al \longrightarrow 2\left(CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O\right)_3Al + 3H_2$

tert- Butyl alcohol. Aluminium tert - butoxide

⊙ 

Sodium phenoxide.

⊙ 

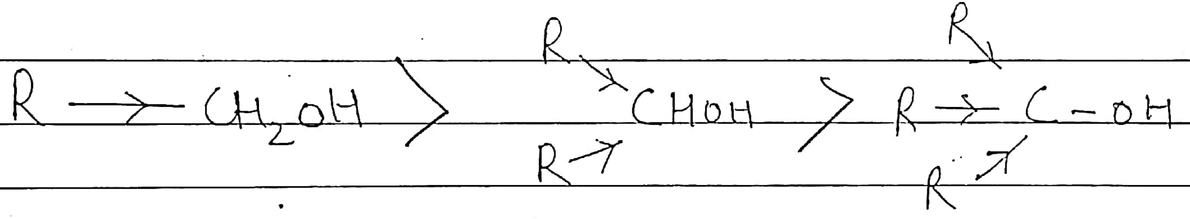
→ The above reaction Show that alcohol and phenol are acidic in nature.

⊙ Alcohal and phenol are Bronsted acid. i.e they Can donate a proton to a Strong base.

$$\bar{B}: + H-\ddot{O}-R \longrightarrow B-H + :\ddot{O}-R$$

Base — Conjugate acid — Conjugate base.

[ii] Acidity of ~~phenol~~ & alcohol: It is due to the polar nature of O-H bond. Presence of e^- donating group ($-CH_3$, $-C_2H_5$) increase e^- density on Oxygen result in decreasing the polarity of OH bond. Hence, decrease the acid strength.



$$R \rightarrow CH_2OH > R_2CHOH > R_3C-OH$$

1° 2° 3°

→ Alcohols are weaker acid than water.

$$R-\ddot{O}:^- + H-\ddot{O}-H \longrightarrow R-O-H + :\ddot{O}H^-$$

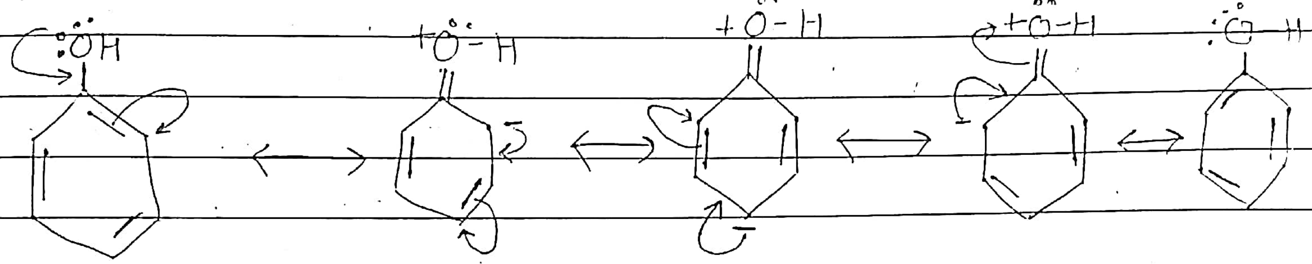
Conjugate acid. Conjugate base

⊙ Alcohol act as Bronstead base as well due to the presence of Unshaired paired e^- on oxygen. which make them proton acceptor.

(iii) Acidity of phenols:

⊙ Hydroxy group is directly attached to Sp^2 hybridis.. Carbon of benzene ring and act as e$^-$ withdrawing group.

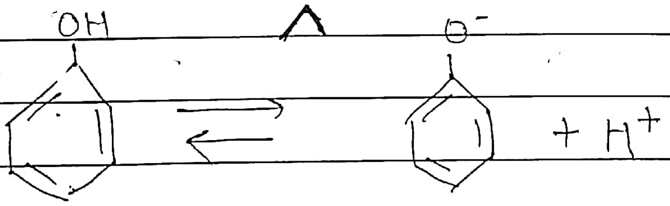
→ Due to charge distribution and its resonance Structure Cause Oxygen of OH group to be positive.



Imp The Rⁿ of phenol with aq.NaOH indicate that phenol are strong acid than alcohol and water.

⊙ Ionisation of an ~~alkoh~~ alcohol and phenol take place as follow:

$$R-\ddot{O}-H \rightleftharpoons R-\ddot{O}:^{-} + H^{+}$$



Due to higher electronegativity of Sp^2 ~~b~~ hybridised Carbon of phenol to which —OH is attached, electron density decr. On Oxygen and incr. the polarity of O-H bond and increase ionisation in phenol that of alcoh alcohal.

→ The presence of e^- withdrawing group such as Nitro group increase the acidic strength of phenol. This effect is more pronounced when such a group is present at Ortho and para positions
(1,2) (1,4)

→ Presence of e^- donating group such as alkyl group. decrease the acidic strength of phenol.

Esterification.

Alcohol and phenol react with Carboxylic acid acid chloride and acid anhydrides to form ester.

⊙ $Ar/R-OH + R'-COOH \underset{\text{Conc. } H_2SO_4}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$

$CH_3OH + C_2H_5COOH \overset{H^+}{\rightleftharpoons} CH_3OCOC_2H_5 + H_2O$

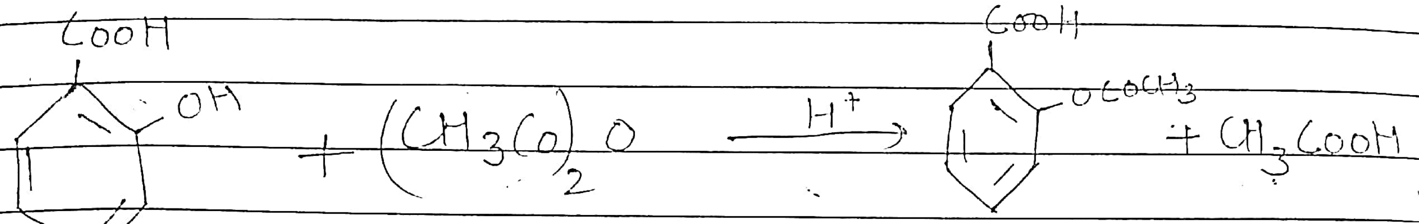
⊙ $Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$

$C_2H_5OH + (CH_3CO)_2O \overset{H^+}{\rightleftharpoons} C_2H_5OCOCH_3 + CH_3COOH$

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

(i) Acetylation of Salicylic acid.

→ Introduction of acetyl (CH_3CO) group in alcohol and phenol is known as acetylation.



Salicylic acid

Acetyl Salicylic acid (Aspirin).

[b] Reaction involving Cleavage of C–O bond in alcohols.

[i] Reaction with hydrogen halides:

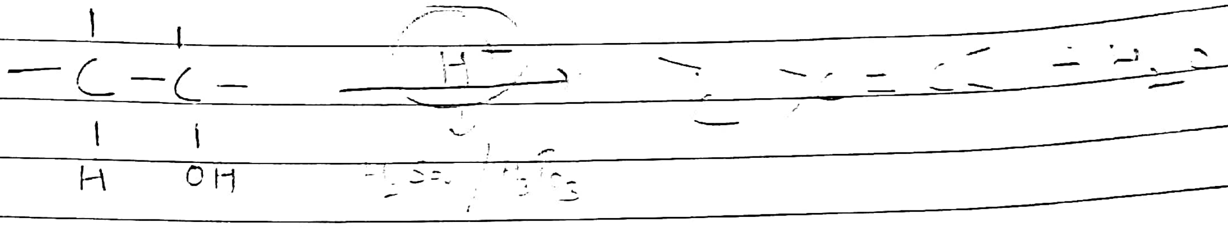
$$ROH + HX \longrightarrow R-X + H_2$$

→ Reactivity of three class of alcohol with HCl distinguishes from Lucas test

Lucas Reagent (Conc. HCl and $ZnCl_2$)

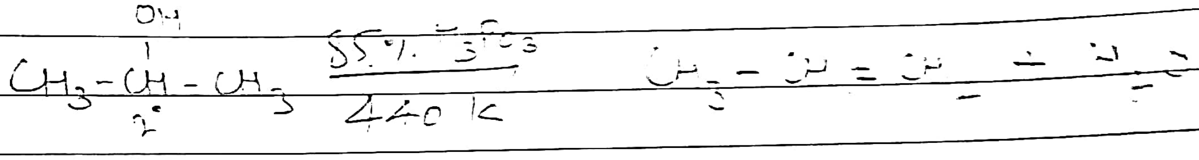
3° alcohol → turbidity produce immediately
2° alcohol → Take Some time.
1° alcohol → do not produce turbidity.

→ Dehydration (loss of water)

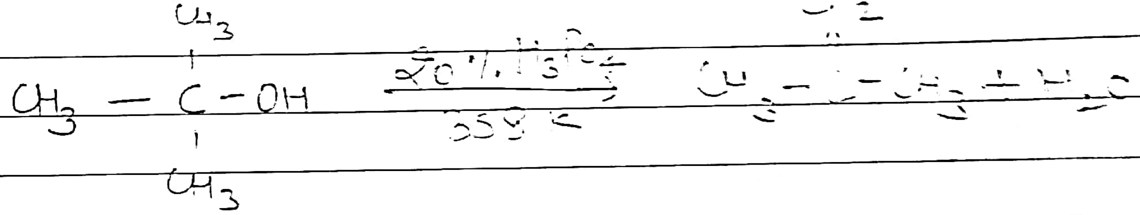


$$-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{OH}{|}}{C}}- \xrightarrow[H_2SO_4/H_3PO_4]{H^+} >C=C< + H_2O$$

⊙ $C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2=CH_2 + H_2O$



⊙ $$CH_3-\overset{\overset{OH}{|}}{\underset{2°}{CH}}-CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

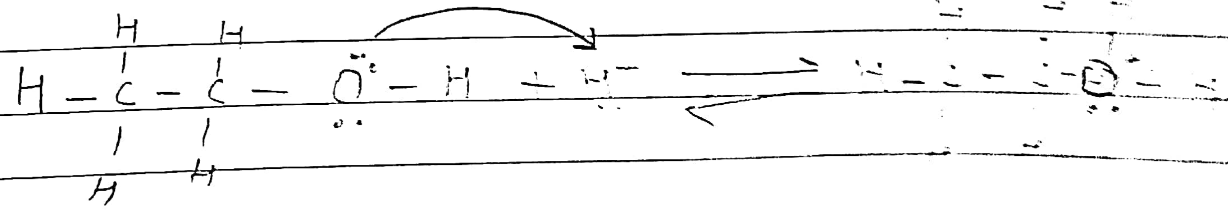


⊙ $$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{\overset{CH_2}{\|}}{C}-CH_3 + H_2O$$

Tertiary > Secondary > Primary

→ Mechanism

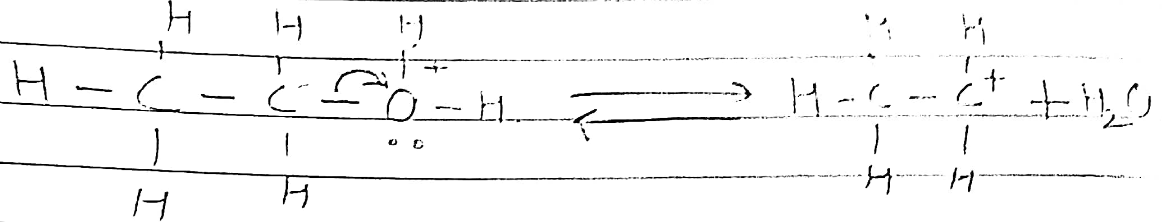
⊙ STEP 1 : Formation of protonated alcohol.



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \rightleftharpoons H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{+}{\underset{\cdot\cdot}{O}}-H$$

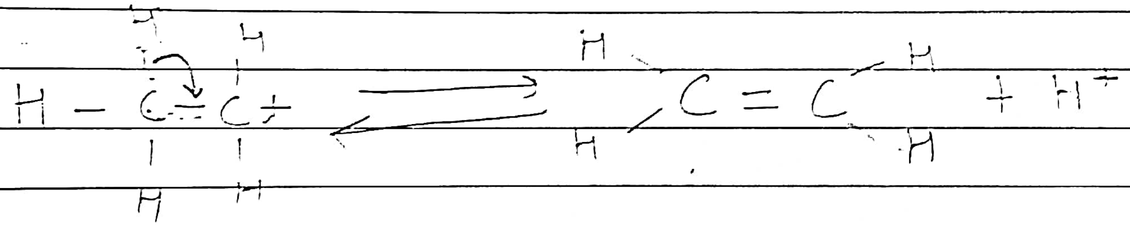
Protonated alcohol
Ethyl Oxonium Ion

STEP 2 : Formation of Carbocation : It is slowest Step and hence, the rate determining Step of reaction.



$H_3C-CH_2-\overset{+}{O}H_2 \rightleftharpoons H_3C-\overset{+}{C}H_2 + H_2O$

STEP 3: Formation of ethene by elimination of a proton.



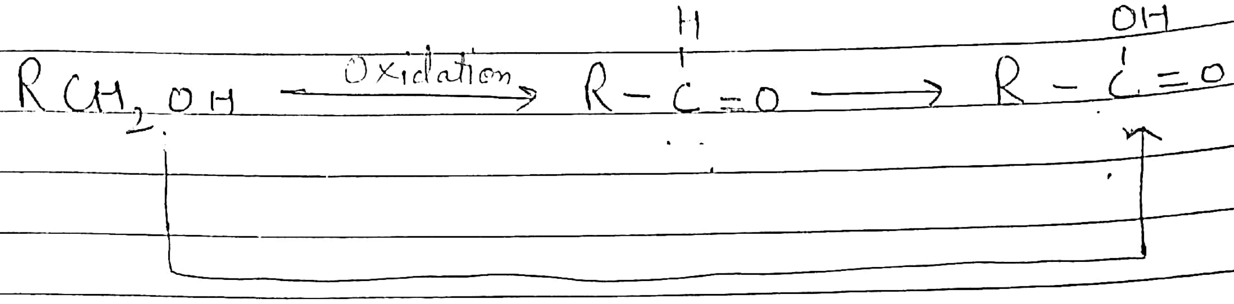
$H_3C-\overset{+}{C}H_2 \rightleftharpoons H_2C=CH_2 + H^+$

⊙ The acid used in Step 1 released & in Step 3.

⊙ Oxidation : involve the formation of Carbon oxygen double bond with cleavage of an O-H and C-H bond.

$H-C-O-H \longrightarrow \;>C=O$

also known as dehydrogenation reaction as loss of dihydrogen from an alcohol.



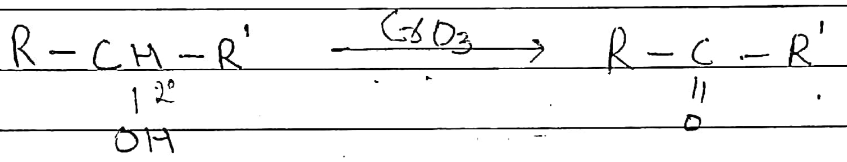
$$RCH_2OH \xrightarrow{Oxidation} R-\overset{H}{\overset{|}{C}}=O \longrightarrow R-\overset{OH}{\overset{|}{C}}=O$$

acidic $KMnO_4$

- $RCH_2OH \xrightarrow{CrO_3} RCHO$
- $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$

Pyridinium chlorochromate

-

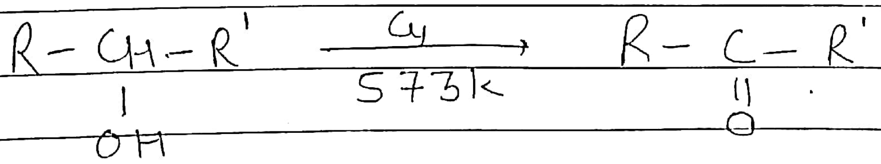


$$R-\underset{\underset{OH}{|}}{CH}-R' \;(2^\circ) \xrightarrow{CrO_3} R-\underset{\underset{O}{\|}}{C}-R'$$

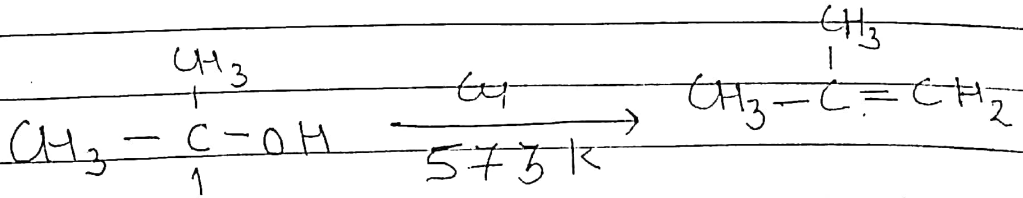
NOTE: 3° Alcohol do not Undergo Oxidation.

- When Vapour of 1° or a 2° alcohol are passed Over heated Cu at 573 K. then.

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



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



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

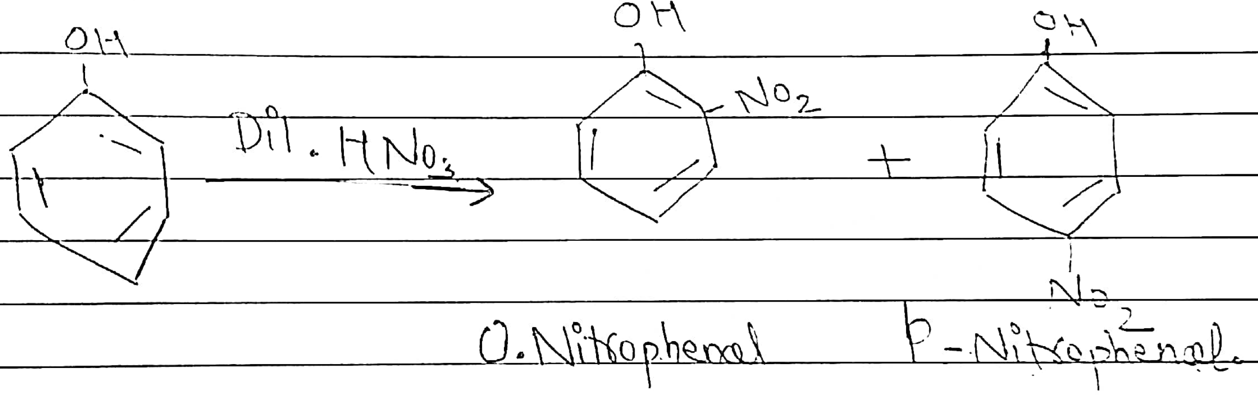
Reactions of Phenols

1. Electrophilic aromatic Substitution.

- The -OH group attached to benzene ring activates it toward electrophilic Substitution.

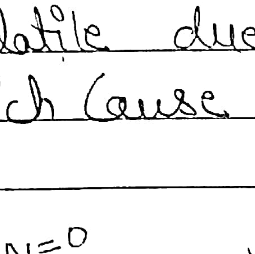
- Also it direct the incoming group to ortho and para possition in ring as these position become electric rich due to resonance effect caused by -OH group

[i] Nitration

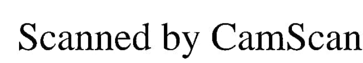


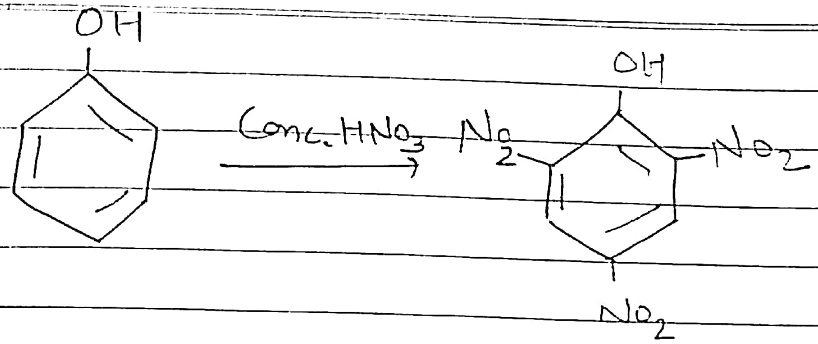
O.Nitrophenol P-Nitrophenol.

→ O-Nitrophenol is Steam Volatile due to intramolecular hydrogen bonding.



→ p-nitrophenol is less Volatile due to intermolecular hydrogen bonding which cause the association of molecule

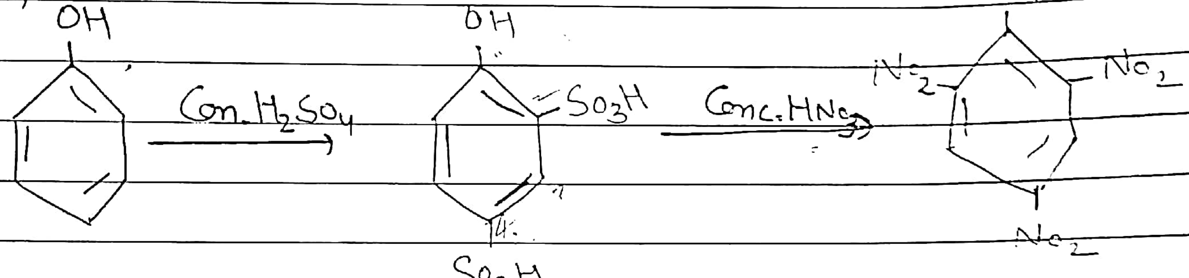




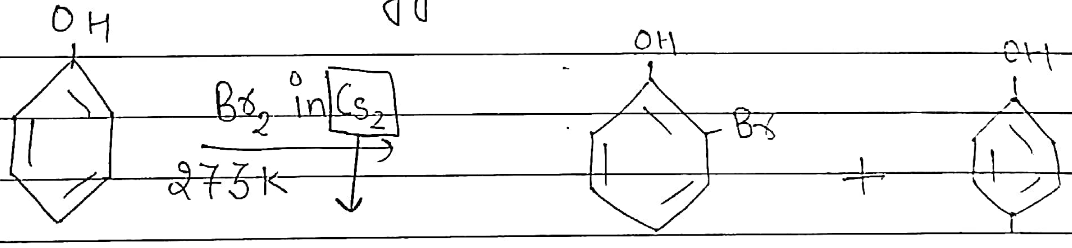
2,4,6 - Trinitrophenol.
(picric acid)

The yield of reaction product is poor.

Nowdays,



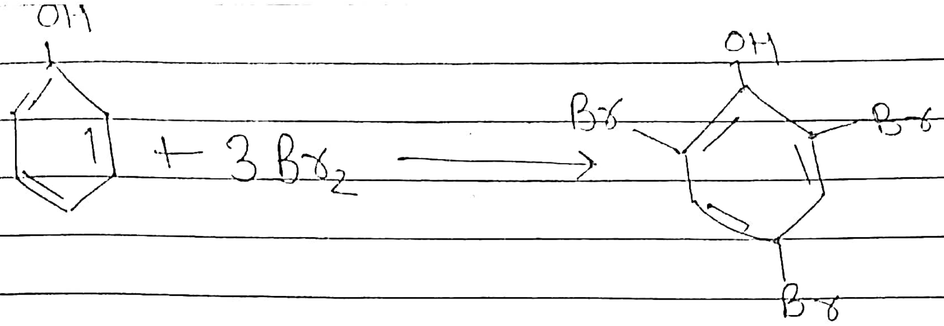
[ii] Halogenations: Treating phenol with bromine different product are formed under different Condition.



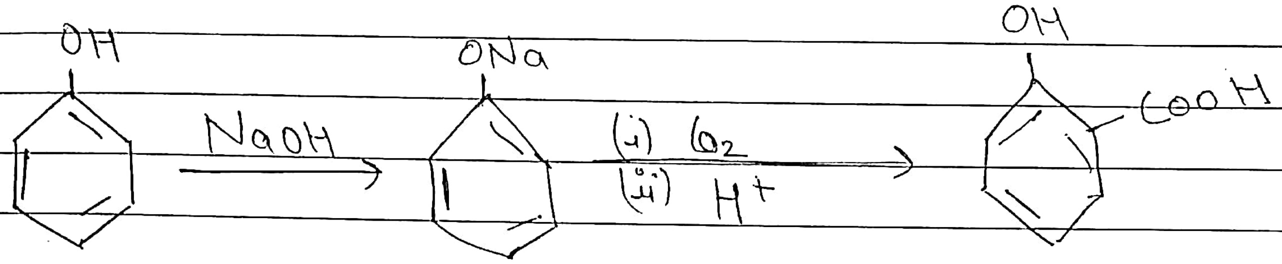
Solvent of low polarity.

Major monobromophenol.

- Halogenation of benzene take place in presence of lewis acid Such as $FeBr_3$, which polarise halogen molecule In Case of phenol polarisation of bromine molecule take place in absence of lewis acid. due to highly activating effect of -OH group.

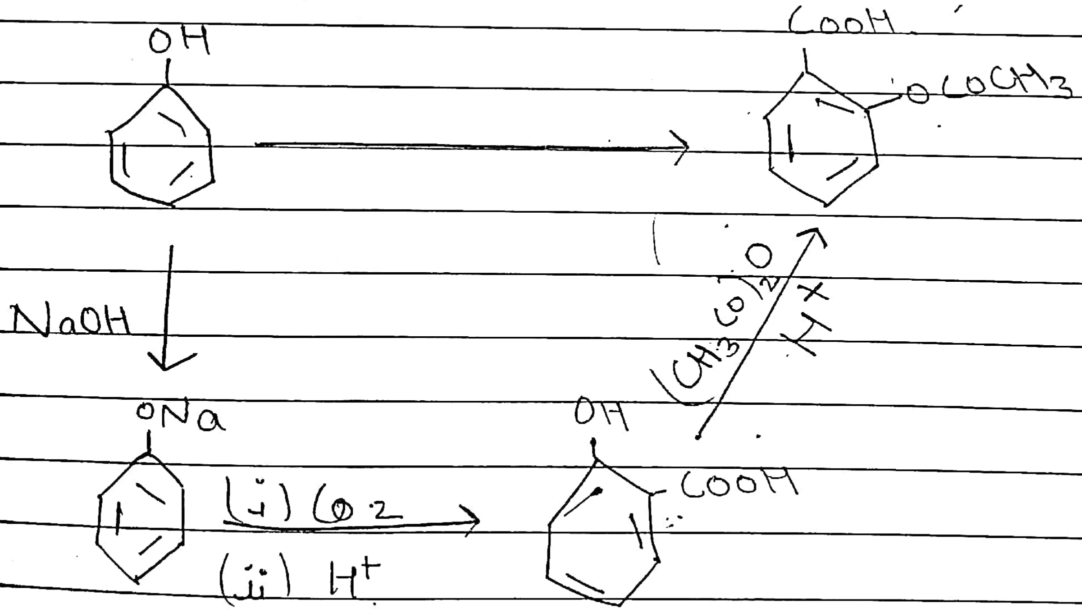


2. Kolbe's reaction

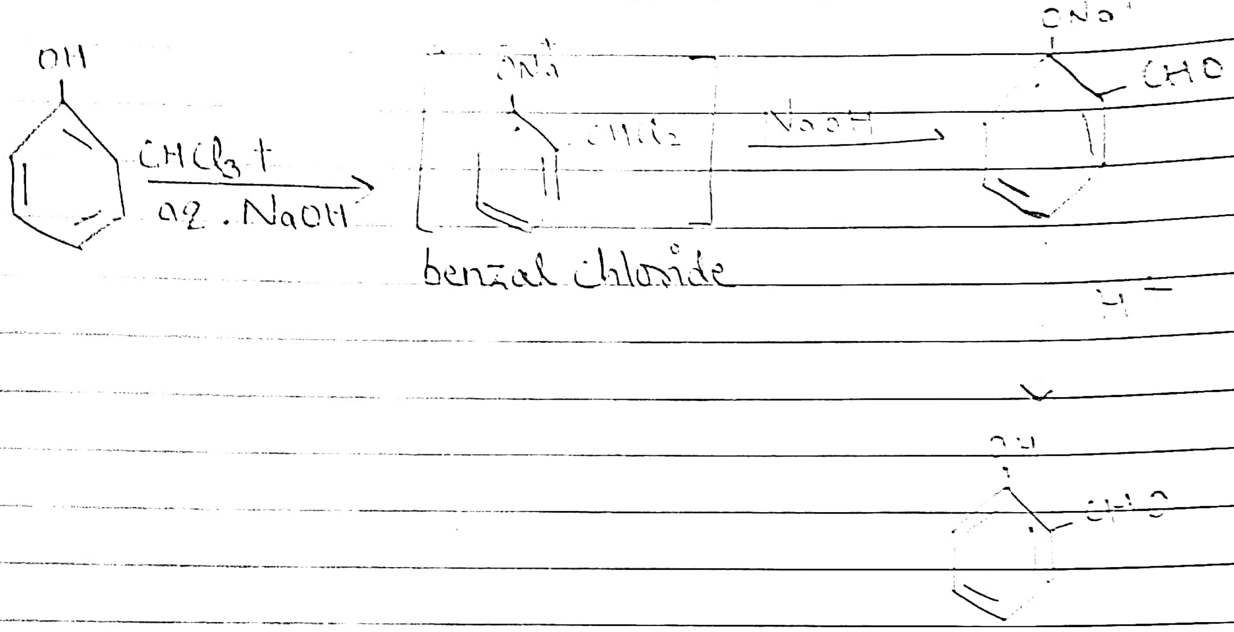


2-Hydroxybenzoic acid
(Salicylic acid)

Q. Convert phenol into Aspirin.



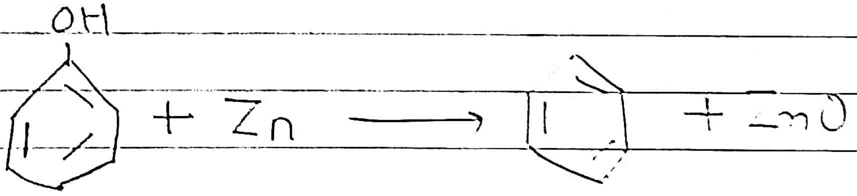
3. Reimer - Tiemann Reaction.



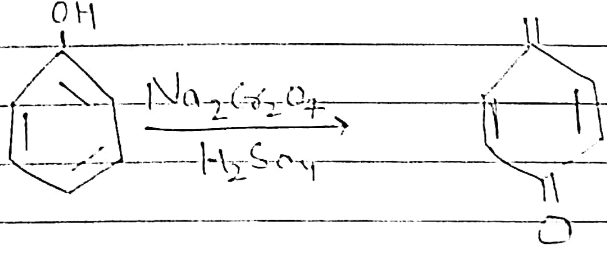
benzal chloride

Salicylaldehyde

4. Reaction of phenol with Zinc dust.



5. Oxidation.



benzoquinone.

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COMMERCIALLY IMPORTANT ALCOHOLS.

1. Methanol.

→ formula - CH_3OH

→ produce by destructive distillation of wood. Today, Methanol is produce by Catalytic hydrogenation of CO at high pressure and temprature in presence ZnO - Cr_2O_3 Catalyst

$$CO + 2H_2 \xrightarrow[\substack{200-300\ atm \\ 573-673K}]{ZnO-Cr_2O_3} CH_3OH.$$

→ It is a Colourless liquid and boil at 337 K.

→ poisnous in nature

→ used as Solvent in paints, Varnishes and for making formaldehyde.

2. Ethanol. [C_2H_5OH]

→ Commercialy produce by Fermentation of Sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\downarrow Zymase$$

$$2C_2H_5OH + CO_2$$

→ Action of Zymase inhibit once the % of alcohol exceed 14%.

→ It is a Colourless and boil at 351 K. used as Solvent in paint industury. Commercially alcohol made Unfit for drinking by adding $CuSO_4$ and pyridine. It is known as denaturation of alcohol.