Alcohols, Phenols & Ethers

Alcohols: Those compounds in which a Hydrogen (more than one) is replaced by -OH group from aliphatic carbons.

$R-OH$

Phenols: when Hydrogen (one or more) is replaced from benzene ring by -OH group.

$Ar-OH$

Ethers: In ethers H is replaced by -OR group where R = alkyl / aryl.

$R-O-R$

$R-O-R'$

CLASSIFICATION :-

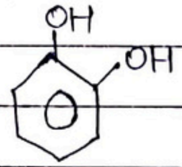
1). On the basis of number of -OH group :

Monohydric (only one -OH group)

CH_3-OH

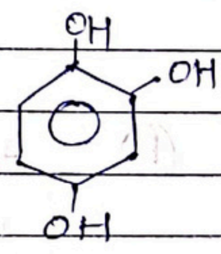
Dihydric (contain 2 -OH group)

CH_2-OH
|
CH_2-OH



Polyhydric (contains more than 2 -OH group)

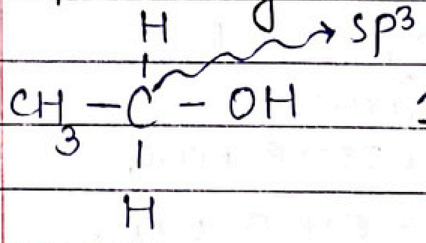
CH_2-OH
|
CH_2-OH
|
CH_2-OH



2) Monohydric compound can be classified as –

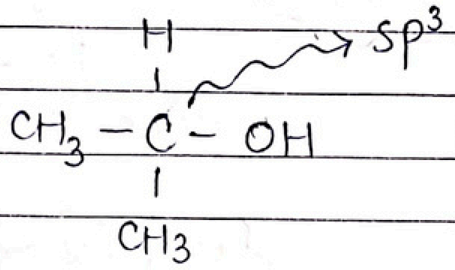
i). Compound containing $C_{sp^3} - OH$ bond :

ⓐ Primary



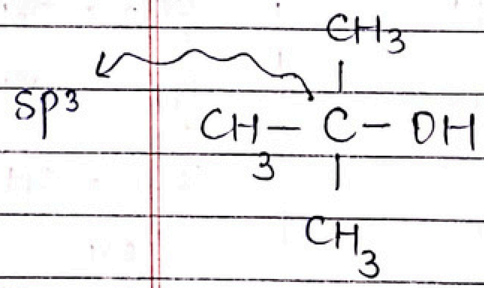
1° alcohol.

Secondary



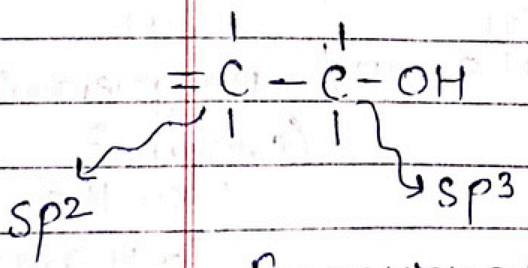
2° alcohol.

Tertiary



3° alcohol.

ⓑ Allylic alcohol



Functional group is attached to sp^3 hybridised C which in turn is attached to sp^2 hybridised carbon.

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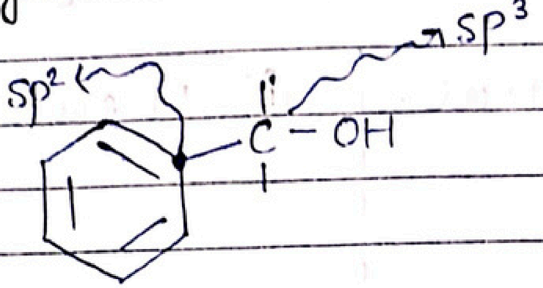
© Benzylic alcohol:



when functional group is attached to a sp^3 hybridised C which is attached to a sp^2 hybridised carbon which belongs to benzene ring.

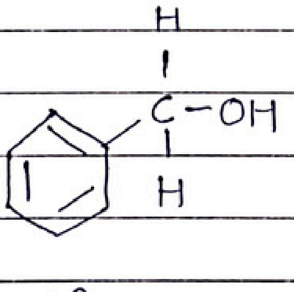
Allylic alcohol can be –

$= \overset{|}{C} - \underset{H}{\overset{H}{C}} - OH$ 1° allylic alcohol

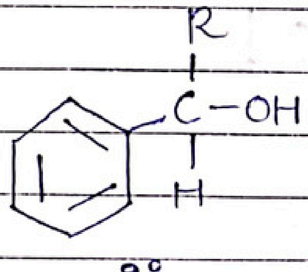
$= \overset{|}{C} - \underset{R}{\overset{H}{C}} - OH$ 2° allylic alcohol

$= \overset{|}{C} - \underset{R}{\overset{R}{C}} - OH$ 3° allylic alcohol.

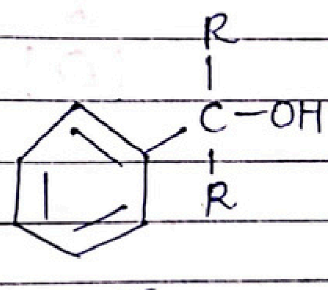
Benzylic alcohol can be –   (R = alkyl/aryl).



1° benzylic alcohol



2° benzylic alcohol



3° benzylic alcohol.

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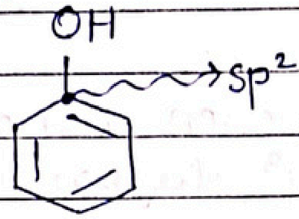
ii) Compounds containing sp^2 hybridised carbon

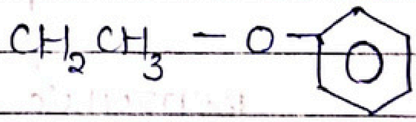
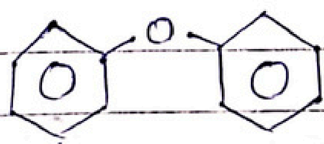
ⓐ Vinylic alcohal.

$$-\overset{|}{C}=\overset{|}{C}-OH \quad (C \rightarrow sp^2)$$

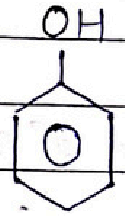
ⓑ Phenols -



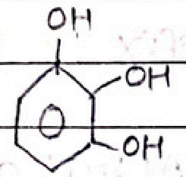
Classification of ethers -

Symmetrical or simple.	Unsymmetrical or mixed
$R-O-R'$	$R-O-R'$
$[R = R']$	$[R \neq R']$
CH_3-O-CH_3	$CH_3-O-C_2H_5$
$CH_3CH_2-O-CH_2CH_3$	
	

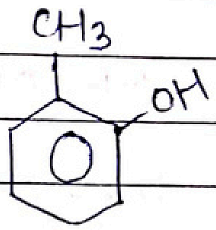
2). Phenols -



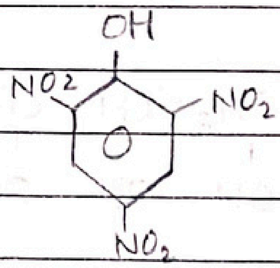
also → carbolic acid.
Phenol ✓
Benzene - 1 - ol

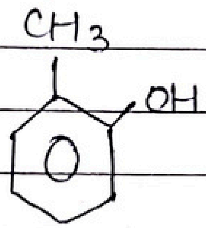


Benzene - 1, 2, 3 - triol
(Pyrogallol)



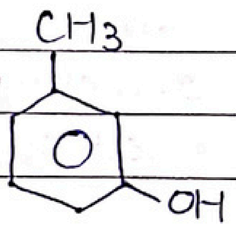
2- methylphenol.
O - cresol



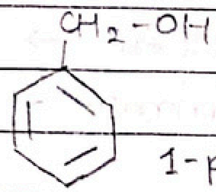


2 - methyl phenol.
O - cresol.

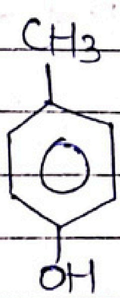
2, 4, 6 - trinitrophenol
(Picric acid)
*



3 - methylphenol.
m - cresol

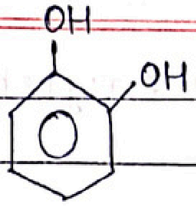


1-phenylmethanol
Benzylalcohol

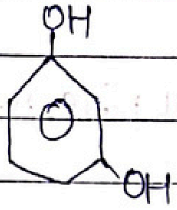


4 - methyl phenol.
p - cresol

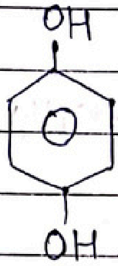
1,2 - Dihydroxybenzene.



Benzene - 1,2 - diol
or
Catechol



Benzene - 1,3 - diol
or
Resorcinol



Benzene - 1,4 - diol
or
* Quinol or Hydroquinone.

3) Ether :

R - O - R

smaller chain: ether functional group. (alkoxy-)

R → longest chain (Alkane). (Parent).

IUPAC: $\boxed{\text{Alkoxy + Alkane}}$

CH_3OCH_3 Dimethylether
Methoxymethane

$C_2H_5OC_2H_5$ Ethoxyethane
Diethylether

$CH_3OCH_2CH_2CH_3$ Methoxy-1-propane
methylpropylether

$C_6H_5OCH_3$ 1-Methoxybenzene.
methylphenylether * Anisole

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$C_6H_5OCH_2CH_3$ Ethylphenylether

1 - ethoxy benzene.

$C_6H_5O(CH_2)_6CH_3$ Heptylphenylether

1 - phenoxyheptane.

$CH_3-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$ methylisopropyl ether.

2 - methoxy propane

$CH_3-CH-CH-CH_3$ (O bridging the two CH)

2,3 - Epoxybutane

$C_6H_5-O-\underbrace{CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3}$

Phenyl isopentyl ether

1-(3-methyl butoxy) benzene.

CH_2-CH_2 (O bridging the two CH_2)

Epoxy ethane

oxirane

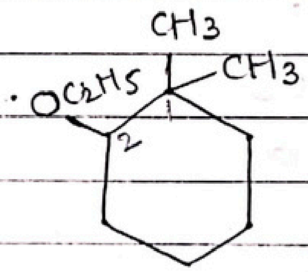
$\underbrace{CH_3-O}-\underset{1}{CH_2}-\underset{2}{CH_2}-\underbrace{O-CH_3}$

1,2 -dimethoxyethane.

$CH_3-CH-CH_2$ (O bridging CH and CH_2)

1,2 - Epoxy propane

or 2-methyl oxirane



2-ethoxy-1,1-dimethylcyclohexane

Common name for ether:

same alkyl group — Dialkylether

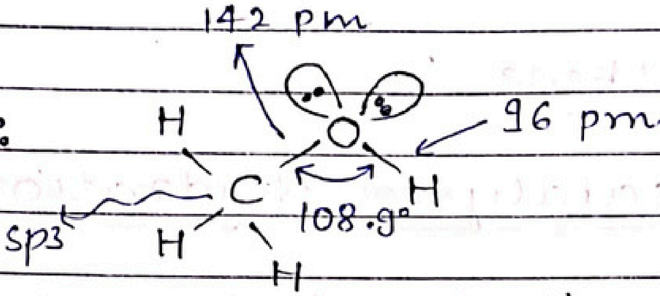
diff. alkyl group. — Alkyl + Alkyl + ether

↓

alphabetically

Structure of Functional Group :-

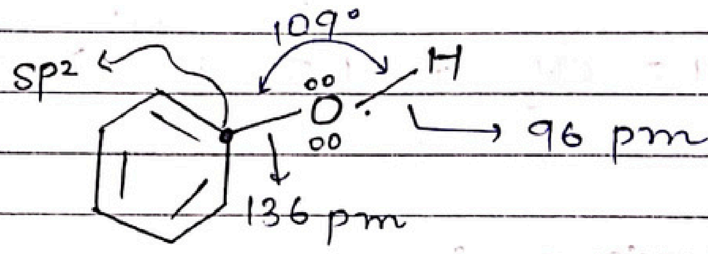
Alcohol:



Tetrahedral

109.5 (but in reality bond angle is less) because of repulsion between lone pair of oxygen and lone pair - bond pair of OH and CO bond.

Phenol:



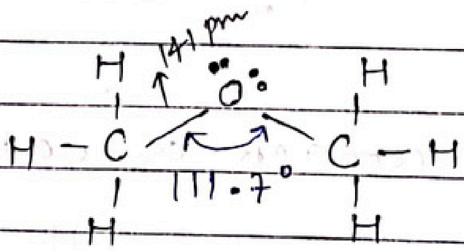
The bond length of C-O in phenol is lesser 136 pm while in alcohol it is 142 pm.

Reason 1). C_{sp^2} in phenol ; ∵ more electronegative bond length decreases.

*

ii). In phenol due to resonance a partial double bond is observed in C-O bond.

Ethers :



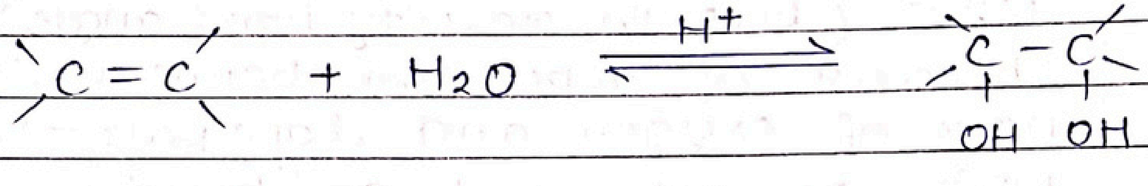
* Bond angle is 111.7° because of its bulky group they repel each other.

Method of Preparations of alcohol :

1) From alkene :

i) By acid catalysed hydration :

↳ Markovnikov's rule & Rearrangment can occur.



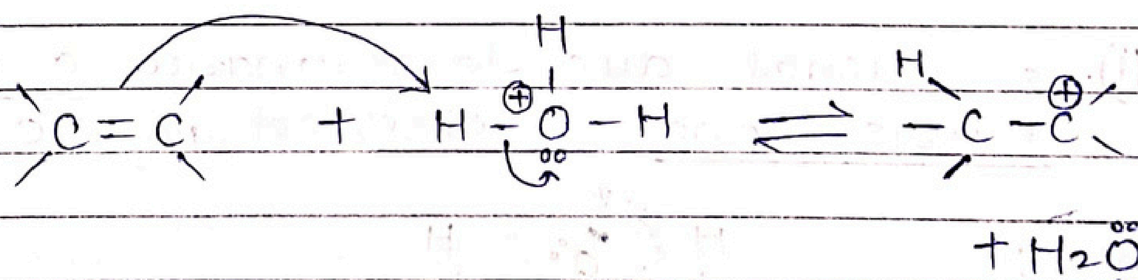
$$CH_3CH = CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3-\underset{\substack{|\\OH}}{CH}-CH_3$$

Mechanism :-

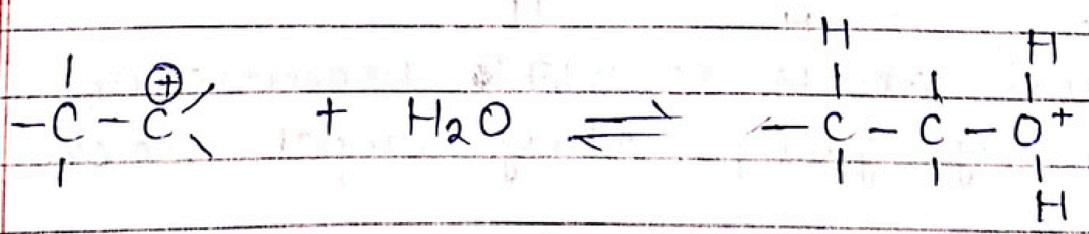
Step①: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$$H_2\ddot{O}: + H^+ \rightleftharpoons H_3\ddot{O}^{\oplus}$$

hydronium ion.



Step②: Nucleophilic attack of water on carbocation



Step 3. Deprotonation to form an alcohol :

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

alcohol.

ii) <u>By hydroboration -oxidation :</u>

Because of presence of peroxide the reaction proceeds through ANTI -MARKOVNIKOV'S RULE.

$$CH_3-CH=CH_2 + (BH_3)_2 \longrightarrow CH_3-CH_2-CH_2-BH_2$$

$$\downarrow CH_3CH=CH_2$$

→ No rearrangement occur

$$CH_3-CH_2-CH_2-\underset{H}{\underset{|}{B}}-CH_2-CH_2-CH_3$$

$$\downarrow CH_3CH=CH_2$$

$$CH_3CH_2CH_2-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CH_3}}{B}-CH_2-CH_2-CH_3$$

$$B(OH)_3 + 3CH_3CH_2CH_2OH \xleftarrow[(H_2O)]{3H_2O_2}$$

3.- Oxymercuration demercuration.
(Markovnikov's rule).
No rearrangement occur.

2. **From carbonyl compounds**

ⓐ **Reduction of aldehyde and ketone :-**

Reducing agent
↳ finely divided Pt, Pd and Ni
↳ $LiAlH_4$
↳ $NaBH_4$

$$\underset{\text{aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} + H_2 \xrightarrow{Pd/Pt/Ni} \underset{(1^\circ)}{R-CH_2-OH}$$

$$\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R} + H_2 \xrightarrow{LiAlH_4} \underset{(2^\circ)}{R-\overset{OH}{\overset{|}{C}}H-R}$$

ⓑ **Reduction of carboxylic acid and ester:**

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2O]{LiAlH_4} R-CH_2-OH$$

↳ $LiAlH_4$ and $NaBH_4$ are expensive reagent.

$$RCOOH \xrightarrow[H^{\oplus},\ -H_2O]{R'OH} \underset{\text{ester}}{RCOOR'} \xrightarrow[\text{catalyst}]{H_2} RCH_2OH + R'OH$$

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[LiAlH_4]{H_2/Pd\ \text{or}} RCH_2OH + R'OH$$

④ $R{-}X + aq.\ KOH \longrightarrow R{-}OH + KX$

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3. ## ★ From Grignard Reagent :-

$$\overset{\delta+}{>C}=\overset{\delta-}{O} + \overset{-\delta}{R}\overset{\delta+}{Mg}X \longrightarrow -\underset{R}{\overset{|}{C}}-O-MgX$$

$$\downarrow H_2O$$

$$-\underset{R}{\overset{|}{C}}-OH + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

(Alcohol)

Formaldehyde -

$$\begin{smallmatrix}H\\H\end{smallmatrix}{>}C=O + CH_3{-}MgCl \longrightarrow H-\underset{CH_3}{\overset{H}{C}}-OMgCl$$

$$\downarrow H_2O$$

$$H-\underset{CH_3}{\overset{H}{C}}-OH \quad 1^\circ \text{ alcohol}$$

$$+$$

$$Mg\begin{smallmatrix}OH\\Cl\end{smallmatrix}$$

It always gives 1° alcohol.

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Aldehyde :

$$\underset{H}{\overset{R}{>}}C=O + CH_3MgBr \longrightarrow R-\overset{H}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OMgBr$$

$$\xrightarrow{H_2O} R-\overset{H}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \text{ (2° alcohol)} + Mg(OH)Br$$

Note: $R = CH_3, C_2H_5, C_3H_7$ etc [except H]

It will give 2° alcohol.

Ketones :-

$$\underset{R'}{\overset{R}{>}}C=O + RMgX \longrightarrow R'-\overset{R}{\underset{R''}{\overset{|}{\underset{|}{C}}}}-OMgX$$

$$\xrightarrow{H_2O} R'-\overset{R}{\underset{R''}{\overset{|}{\underset{|}{C}}}}-OH + Mg(OH)X$$

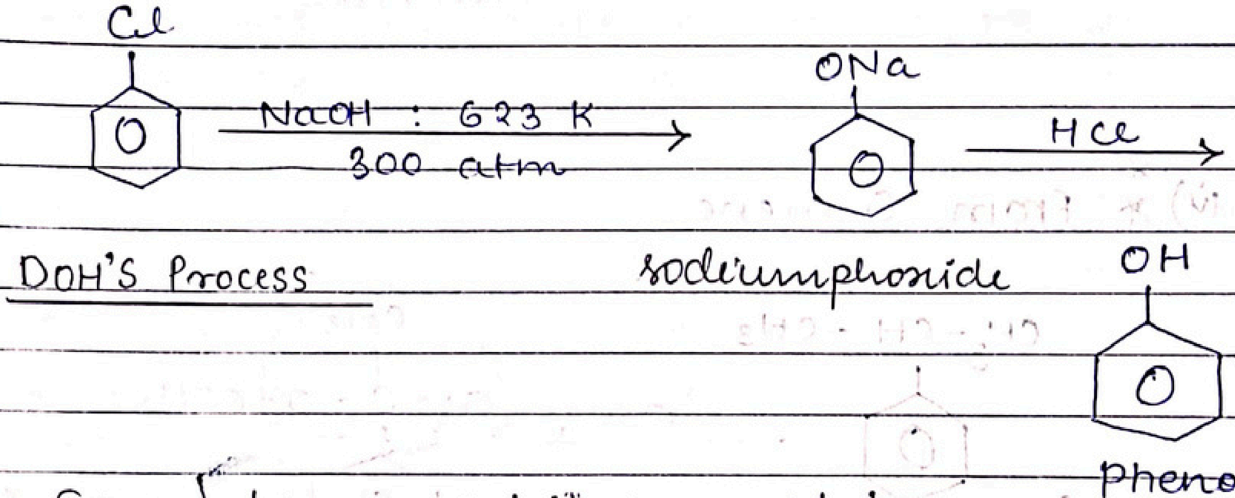
(3° alcohol).

Grignard reagent with ketone gives tertiary alcohol.

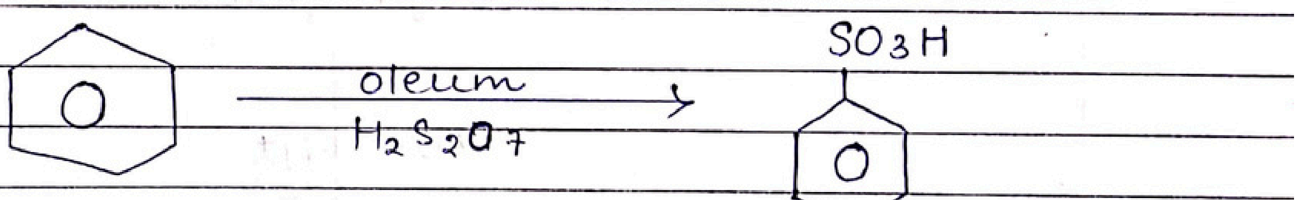
Preparation of Phenols :-

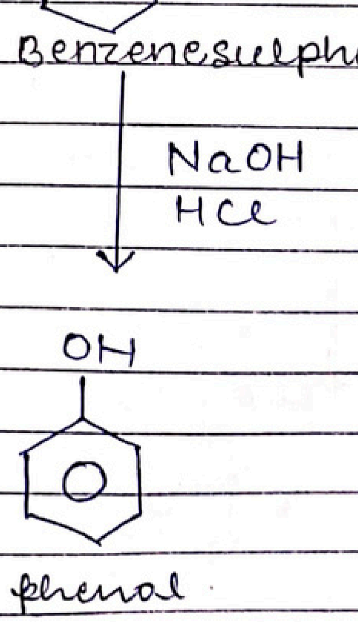
Phenol is also known as carbolic acid was first prepared from coal Tar in early 19th century.

i). From haloarenes :



ii) From benzesulphonic acid :

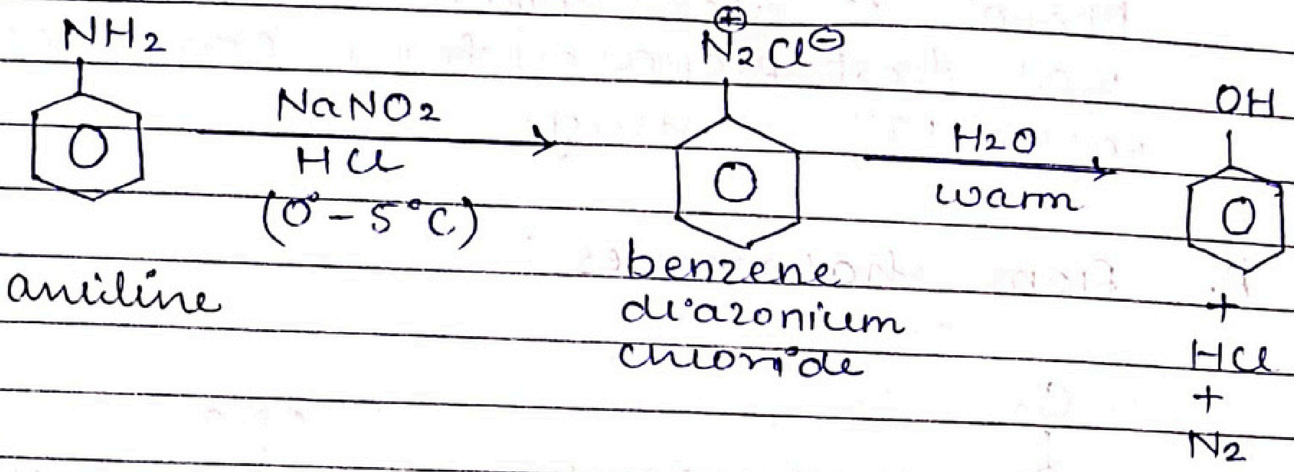




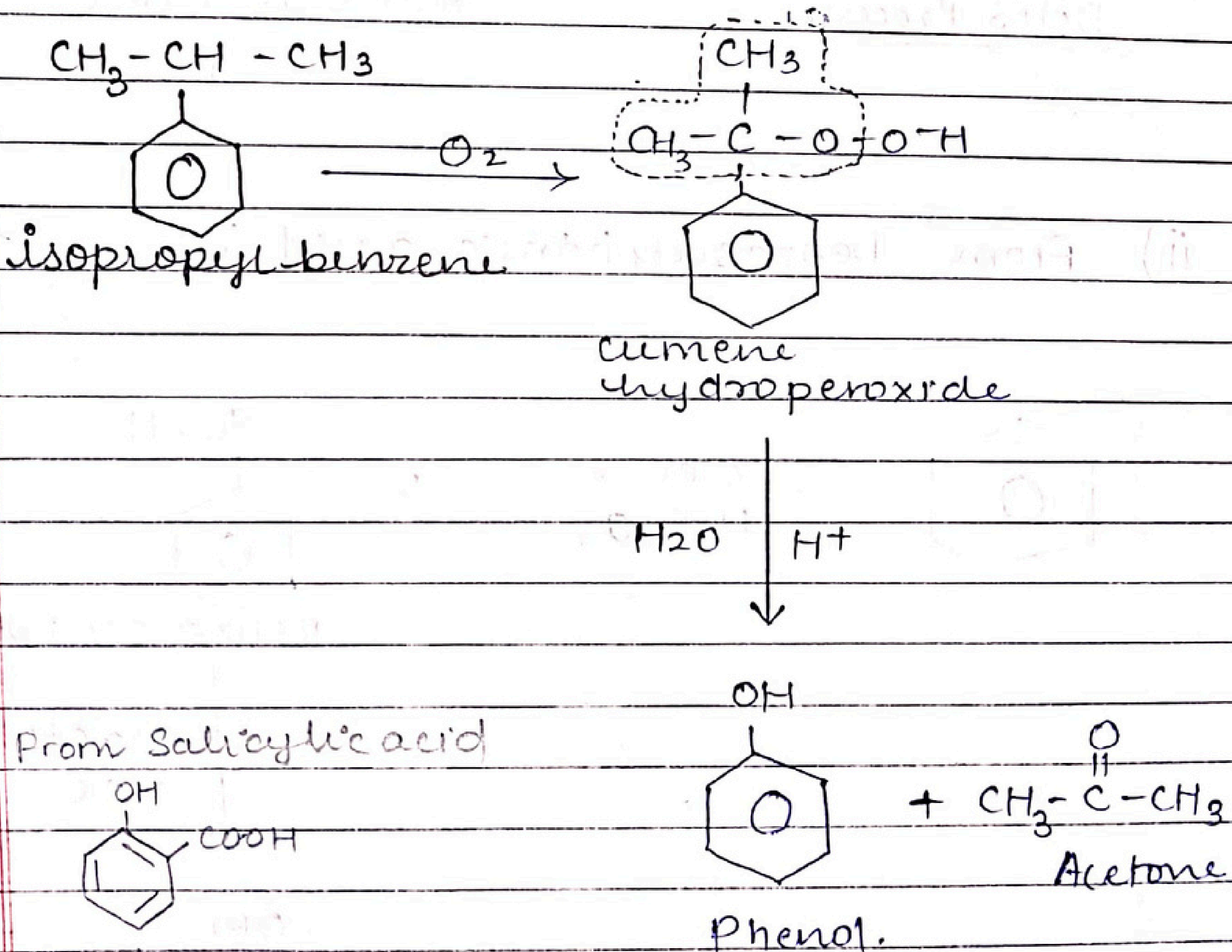
Name reaction.

* Doh's process
* Lucas Test
* Kolbe's Reaction
* Reimer Tiemann rxn
* Williamson Synthesis

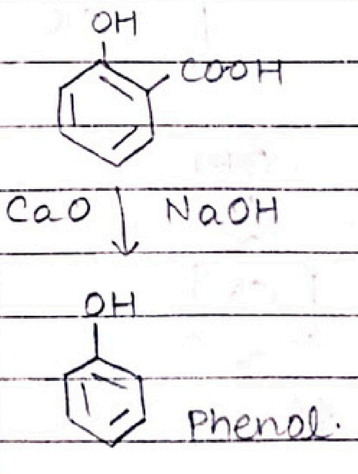
iii) From aniline (benzene diazonium halides)



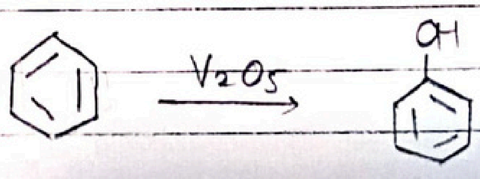
iv) * From Cumene



* From Salicylic acid



* from Benzene



Physical Properties :-

1) Boiling point :$\propto$ Molecular mass
As the number of C ↑ses in alcohol
(Vanderwaal ↑) [surface area ↑]
∴ Boiling point ↑ increases.

but if branching increases in alcohol then boiling point decrease because decrease in surface area.

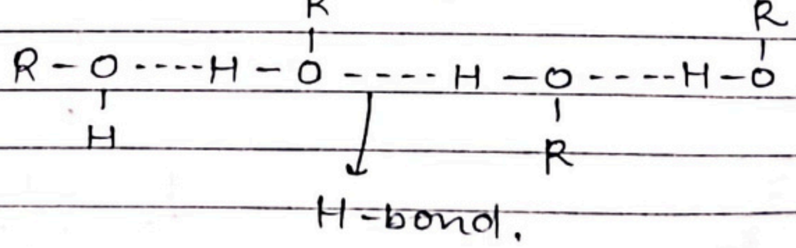
As compared to other compound like haloalkane and haloarenes, hydrocarbon, ethers etc. of comparable mass, alcohol and phenols have more boiling point.

ethanol		propane
CH_3CH_2OH	>	$CH_3CH_2CH_3$
(44)		(44)
351 K		231K

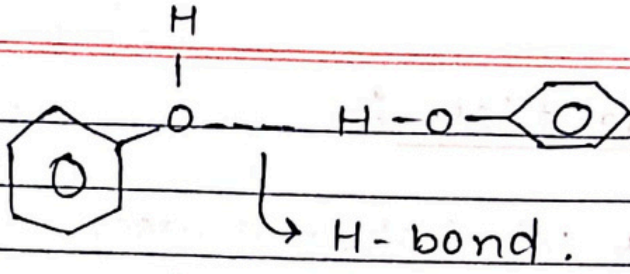
$B.P \propto \frac{1}{Branching}$

CH_3-O-CH_3 ether
methoxymethane
(46) 248 K

Reson - Alcohol and phenals have intermolecular Hydrogen Bonding.



H-bond.



ii) Solubility : Alcohol and phenols.

Lower alcohols (Lesser molecular mass) are easily soluble in H_2O in any proportion because of H-bonding.

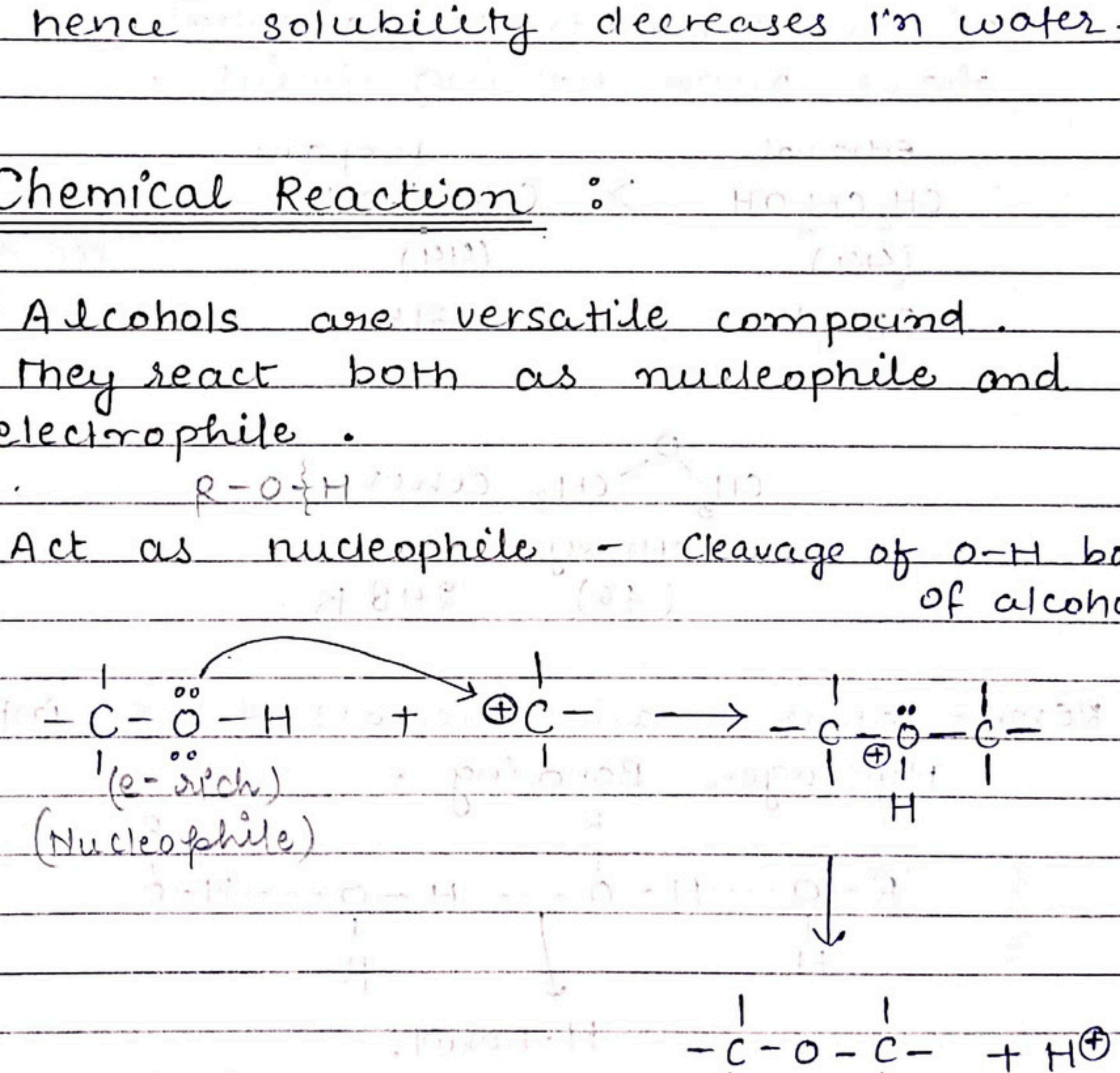
As the no. of carbon increases in alcohol (R = alkyl / aryl group) are hydrophobic in nature. hence solubility decreases in water.

Chemical Reaction :

Alcohols are versatile compound. They react both as nucleophile and electrophile.

R–O{H

▶ Act as nucleophile – Cleavage of O–H bond of alcohol.



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$R - O - H$

- Act as electrophile: cleavage of C–O bond of alcohol.

$$-\overset{|}{\underset{|}{C}}-\ddot{\underset{..}{O}}-H \quad + \quad H^{+} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{..}{O^{\oplus}}}-H$$

e⁻ deficient species electrophile

$$\downarrow$$

$$:Br^{-} \quad \overset{\oplus}{C}- \quad + \quad H_2O$$

$$\downarrow$$

$$-\overset{|}{\underset{|}{C}}-Br.$$

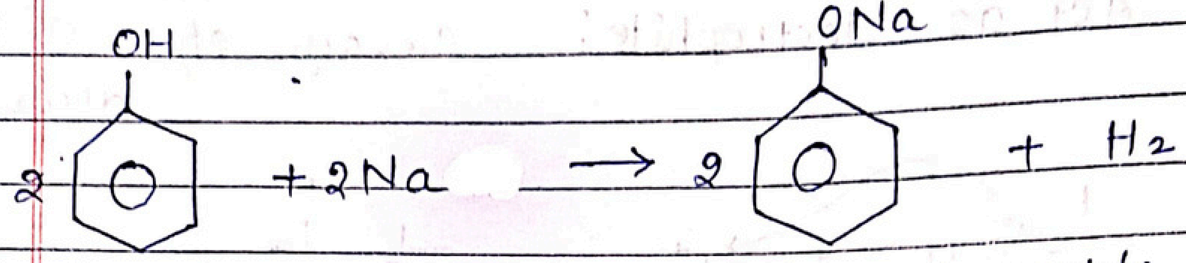
ⓐ Reaction involving cleavage of OH bond of alcohol and phenol (Nucleophile):-

1. Acidic nature of alcohol and phenol.

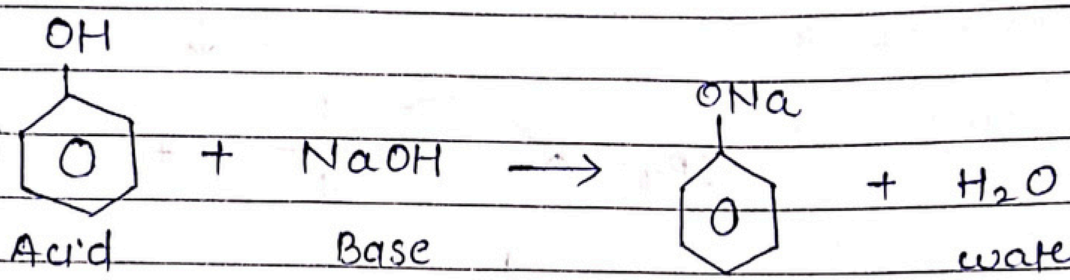
$$2R-\ddot{\underset{..}{O}}-H \quad + \quad 2Na \longrightarrow 2R-\ddot{\underset{..}{O}}-Na \quad + \quad H_2\uparrow$$

acid   metal   Sodium alkoxide

metals use Na, K, Al



phenol Sodium phenoxide



Acid Base Salt water

Acid and phenols are donating H^+ to a strong base.
∴ They behave as BRONSTED ACID.

$$R-\ddot{\underset{\cdot\cdot}{O}}-H + :B^{\ominus} \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}^{\ominus} + BH$$

Bronsted Acid | Bronsted Base | conjugate base | conjugate acid

ii) Acidity of alcohols :

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH > R'-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-OH > R'-\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}-OH$$

1° 2° 3°

less polar OH bond

① Phenol > CH_3OH > water > other alcohol

② Acidic strength $\propto \dfrac{-I \text{ effect (EWG)}}{+I \text{ effect (EDG)}}$

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As the number of alkyl group (e⁻ donating group) increase in C of alcohol, they releases their e⁻ density towards C and ∴ O−H bond polarity decrease and release of proton also decrease hence acidity decreases.

$$R-\ddot{\underset{\cdot\cdot}{O}}^{\ominus} + H-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-H + {}^{\ominus}\ddot{\underset{\cdot\cdot}{O}}H$$

Bronsted base — Bronsted acid — conjugate acid — conjugate base

* H_2O is a stronger acid than ROH.

* $RO^{\ominus}$ is a stronger base than $OH^{\ominus}$

Alcohols acts as Bronsted bases as well. It is due to the presence of unsharred electron pair on oxygen, which make them proton acceptor.

Hence, Alcohol acts as Bronsted Acid (H^+ donor) as well as Bronsted Base (H^+ acceptor).

Alcohol → $R-OH \longrightarrow R-O^{\ominus} + H^+$ (+I)

water → $H_2O \longrightarrow H^+ + OH^{\ominus}$

Alcohol is less acidic than H_2O.

Acidity Phenol > CH_3OH > water > other alcohol.

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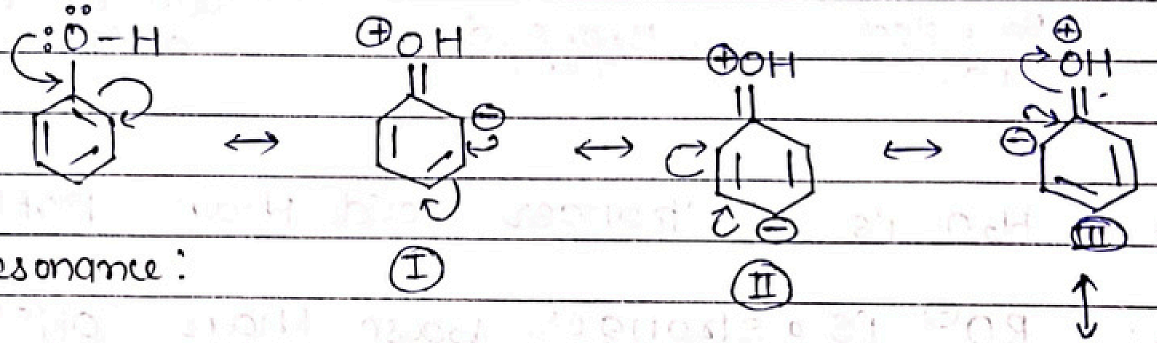
iii) Acidity of phenols :

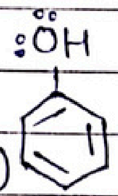
* Phenols are comparatively stronger acids as compared to alcohol and water (releases H^+ easily).

$$CH_3-\ddot{\underset{..}{O}}-H \rightarrow CH_3-\ddot{\underset{..}{O}}^{\ominus} + H^{\oplus}$$

[Alkoxide ions are less stable.]

Due to Resonance :





-OH group in phenol is attached to a more electronegative carbon (sp^2)

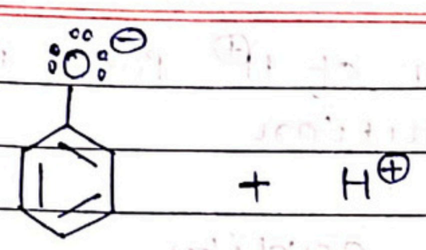
therefor, e^- density on oxygen decreases

Hence, polarity of O-H bond increases.

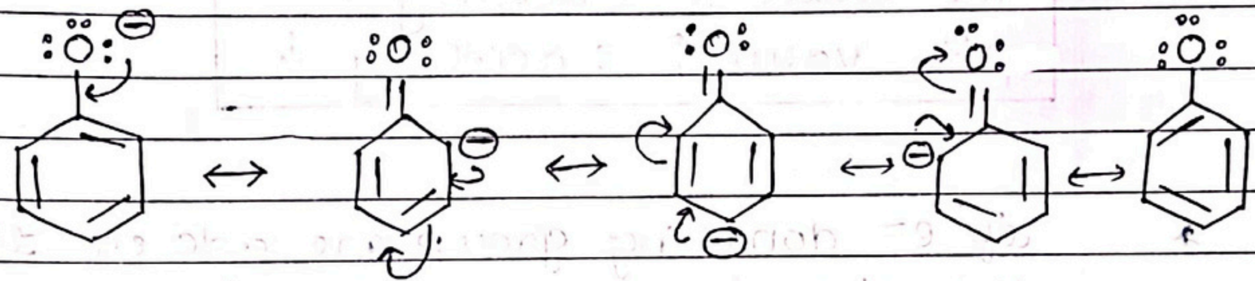
Oxygen will attract the electron of hydrogen towards itself therefore it releases proton easily.

Therefore making phenol acidic.

→ As compared to alkoxide ions phenoxide are more stable.



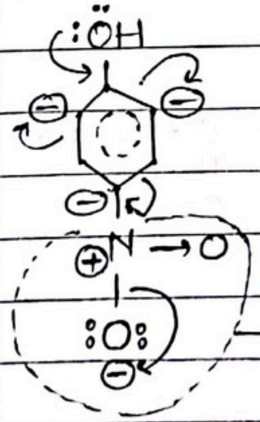
Phenoxide ions.



↳ charge delocalisation is observed in phenoxide ion ∵ making it very stable.

In phenal molecule 'charge separation' is observed which makes its less stable whereas in phenoxide ion no charge separation, hence it is more stable.

★ Electron withdrawing group increases acidity of phenol i.e. less pK_a ↓; more acidity ↑.



→ e⁻ withdrawing group.

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Acidity : concentration of $H^{\oplus}$ ions in a solution.

more H^+ conc. ; more acidity

K_a value ↑ : acidity ↑
pK_a value ↑ ; acidity ↓

* if e^- donating group are added to the phenol, causes the increase in e^- desity in ring therefore less polarity of OH bond and hence acidity decreases.

2. Esterification : $\left[R-\overset{O}{\overset{\|}{C}}-O-R' \right]$ ester.

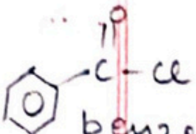
* ($1° > 2° > 3°$)

(R = alkyl / aryl group)

$$R-OH \; + \; \underset{\text{carboxylic acid}}{R-\underset{O}{\underset{\|}{C}}-O-H} \; \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} \; H_2O + \underset{\text{ester}}{R-O-\underset{O}{\underset{\|}{C}}-R'}$$

$$R-OH \; + \; \underset{\text{acid anhydride}}{\begin{matrix} R-\overset{O}{\overset{\|}{C}} \\ \quad\;\; O \\ R-\underset{O}{\underset{\|}{C}} \end{matrix}} \; \overset{H^+}{\rightleftharpoons} \; \underset{\text{ester}}{R-O-\underset{O}{\underset{\|}{C}}-R'} + R-COOH$$

↳ Remove the water and carboxylic acid continuously as the reaction is reversible.



benzenoylchloride

$CH_3-\underset{\overset{||}{O}}{C}-Cl$ ethanoyl chloride

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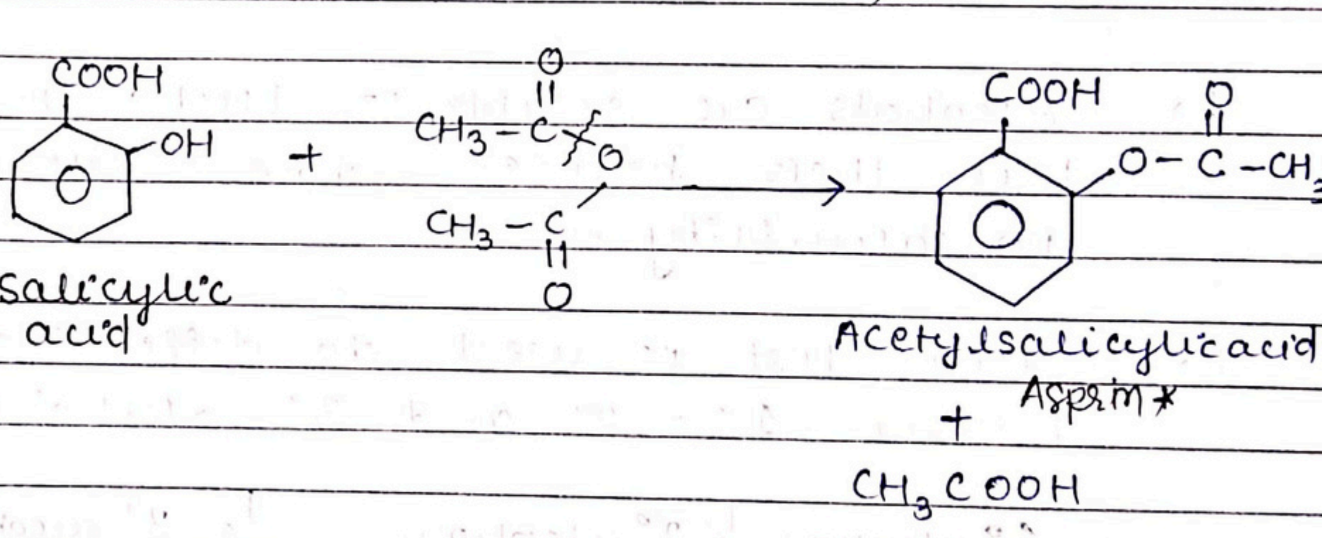
$R-OH + R-\underset{\overset{||}{O}}{C}-Cl \xrightarrow{\text{Pyridine}}$ HCl + $R-\underset{\overset{||}{O}}{C}-O-R$

acid chloride or acylchloride — ester.

↳ Pyridine is basic in nature and used to neutralise the reaction medium because HCl is being produced.

★ Acetylation : Process of addition of acetyl group $\left(CH_3-\overset{O}{\overset{||}{C}}-\right)$



Salicylic acid

Acetylsalicylic acid
Asprin*

+

CH_3COOH
(ethanoicacid)

Aspirin : Acetylsalicylic acid

↳ PAIN killer
↳ Anti - inflammatory
↳ Reduce fever.

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(b) Reaction involving cleavage of C-O bond (electrophile) :-

1) Reaction with Hydrogen halide:
($X = Cl, Br, I$)

$$R\text{-}OH + HX \xrightarrow{ZnCl_2} RX + H_2O$$

alkyl halide.

* LUCAS TEST :- Groove's Process

→ Lucas reagent is a mixture of concn. HCl and $ZnCl_2$.

↳ Alcohols are soluble in Lucas reagent but their halides shows difference in solubility.

↳ Lucas test is used to differentiate between 1°, 2° and 3° alcohols.

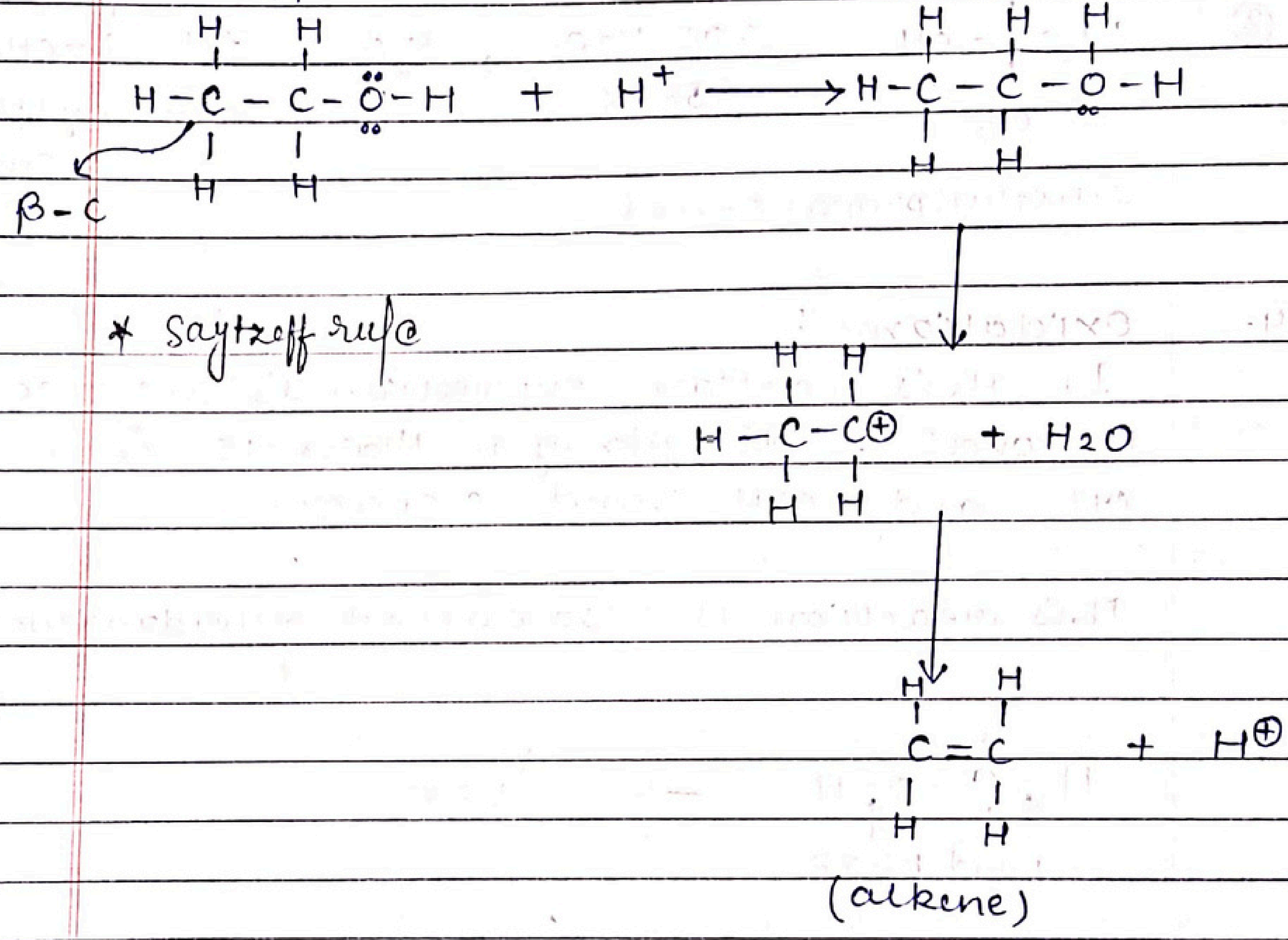
1° alcohol	< 2° alcohol	< 3° alcohol.
↓	↓	↓
Lucas reagent	Lucas reagent	Lucas reagent
↓	↓	↓
RX (1° alkyl halide)	RX (2° alkyl halide)	RX (3° alkyl halide)
NO TURBIDITY	Turbidity appears after few minutes	Instantly Turbidity

$ROH + PCl_5 \longrightarrow RCl + HCl + POCl_3$

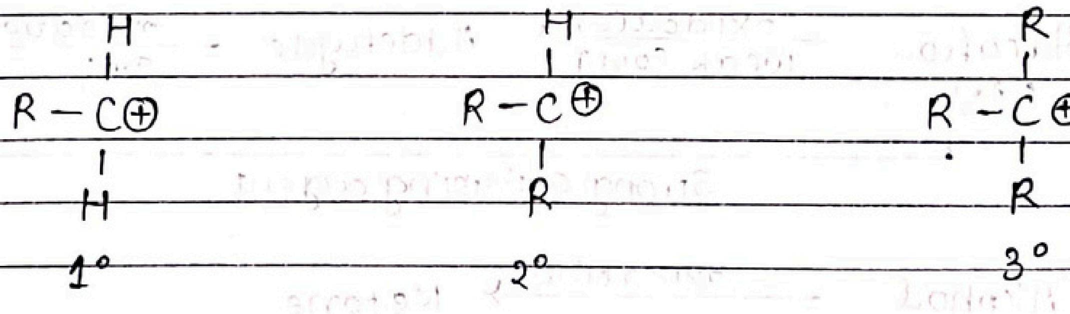
2. Reaction with phosphorus trihalide :

$PCl_3 + 3ROH \rightarrow 3R-Cl + H_3PO_3$

3. Dehydration : (conc. H_2SO_4 and H_3PO_4)
(β - elimination reaction)



* Saytzeff rule



$3° > 2° > 1°$

3° alcohols are more reactive toward this reaction.

Acid should be Protic acids.

① $CH_3CH_2-OH \xrightarrow[443\ K]{H_2SO_4} H_2O + CH_2=CH_2$

ethanol — ethene.

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

propan-2-ol — propene.

③ $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} H_2O + CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

2-methylpropane-2-ol — 2-methylprop-1-ene.

4. Oxidation :

In this reaction oxidation is absorbed by removal of dihydrogen that is from OH and C-H bond cleavage.

This reaction is also called dehydrogenation.

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

↑ ↑
Bond break

$\underset{(1°)}{\text{Alcohol}} \xrightarrow[\text{weak [O.A]}]{\text{oxidation}} \text{Aldehyde} \xrightarrow[\text{[OA]}]{\text{oxidation}} \text{carboxylic acid}$

Strong oxidising agent

$\underset{(2°)}{\text{Alcohol}} \xrightarrow{\text{oxidation}} \text{Ketone}$

$\underset{(3°)}{\text{Alcohol}} \xrightarrow{\text{oxidation}}$ usually Alkene or small carboxylic acid.

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weak oxidising agent · · Strong oxidising A.

- Pyridine chlorochromate (good yeild) - Alk. $K_2Cr_2O_7$
- Fehling's reagent - acidified $KMnO_4$
- Tollen's Reagent - Jonez Reagent
- CrO_3 ($CrO_3 + H^+ +$ acetone)
- POT
- Collin's Reagent

$$R-CH_2OH \xrightarrow[\text{[O·A]}]{\text{weak}} R-CHO \xrightarrow{\text{oxid}^n} RCOOH$$

aldehyde — carboxylic acid

$$R-\underset{\substack{|\\H}}{CH}-CH_3 \xrightarrow[CrO_3]{O \cdot A} R-\underset{\substack{\|\\O}}{C}-CH_3$$

ketone.

3° alcohol do not under oxidation to give aldehyde or ketone.

because of unavailable H (C-H) it do not take place.

⇒ In extreme condition like high temp, high pressure and strong oxidising agent the 3° alcohol break into smaller C unit and hence smaller carboxylic acids are formed.

$$CH_3-CH_2-OH \xrightarrow[573\,K]{Cu} CH_3-CHO$$

aldehyde

$$CH_3-\underset{\substack{|\\OH}}{CH}-CH_3 \xrightarrow[573\,K]{Cu} CH_3COCH_3$$

ketone

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

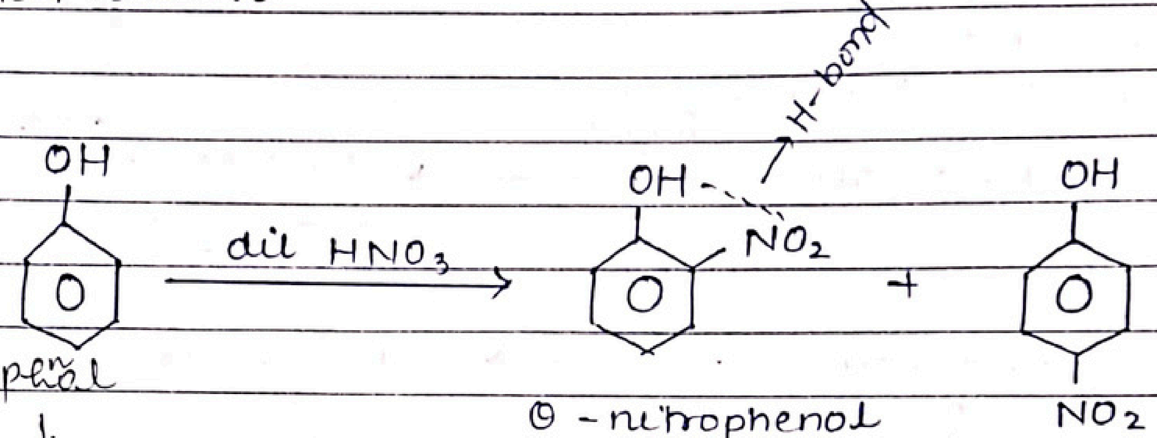
alkane.

β-elimination.

Reactions of phenols :

1) Electrophilic aromatic substitution reaction

(a) Nitration



phenol
↓
Highly activating and o/p-directing

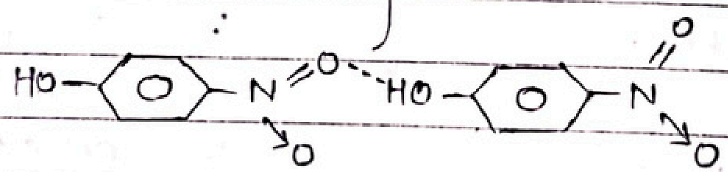
O-nitrophenol
major
↓
due to presence of H-bonding between OH and NO_2 group.
[intramolecular H-bonding]

p-nitrophenol
minor

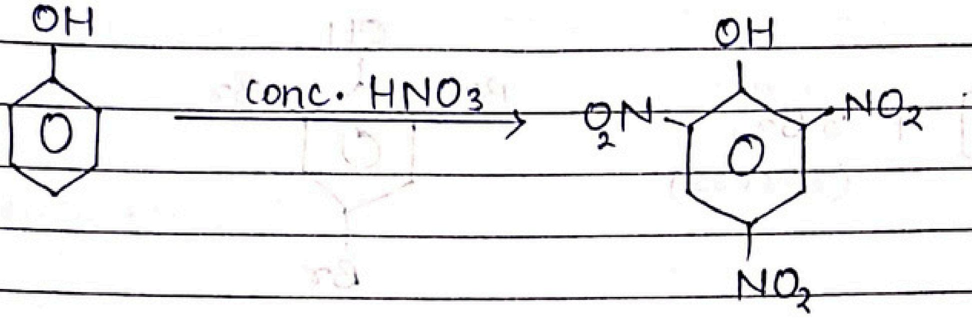
* ↳ O-nitrophenol is having less boiling point than p-nitrophenol. Hence, this mixture can be easily separated.

Reason :

H-bond (intermolecular)

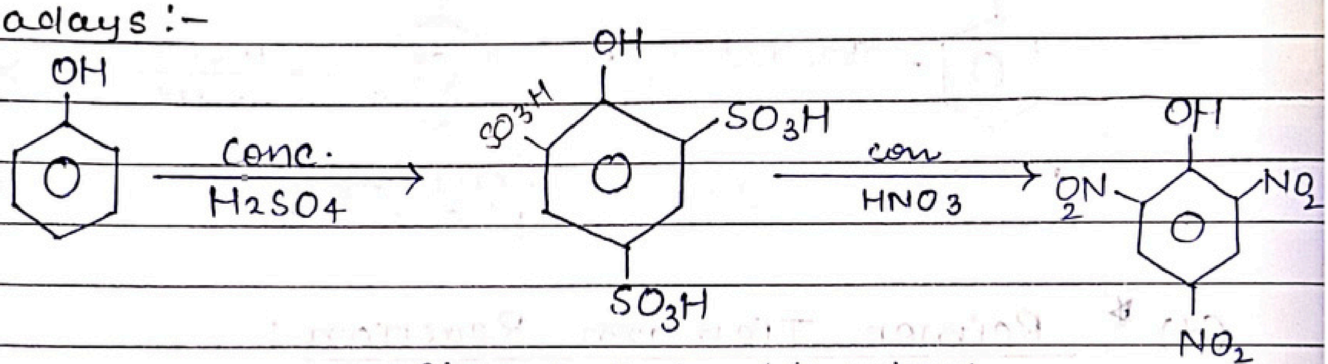


↳ p-nitrophenol have intermolecular H-bonding but O-nitrophenol have intramolecular H-bonding.



2,4,6-trinitrophenol
* (Picric acid)

Nowadays :-

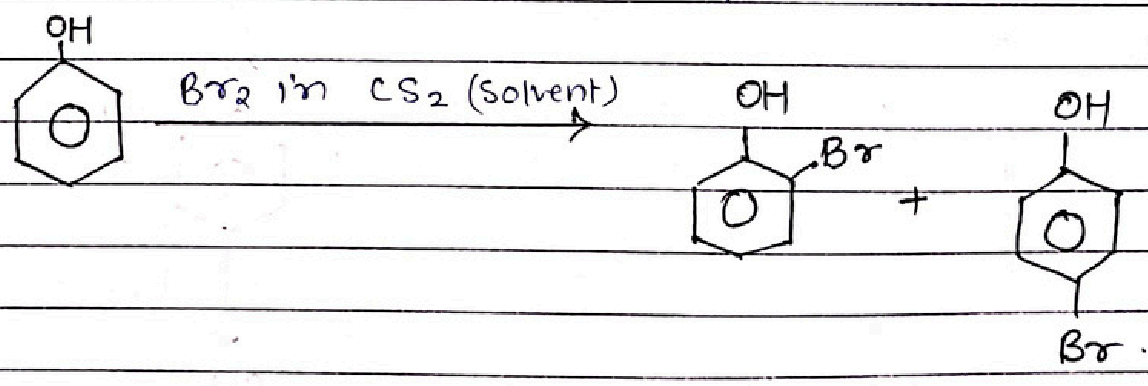


Phenol-2,4-disulphonic acid

Picric acid

(b) Halogenation :

* Generally for halogenation like in bezene, lewis acid like $FeBr_3$, $FeCl_3$, $AlCl_3$ etc. are used to create X^+ electrophile, but phenol is already very active because of -OH group.
∵ Lewis Acid are not required.



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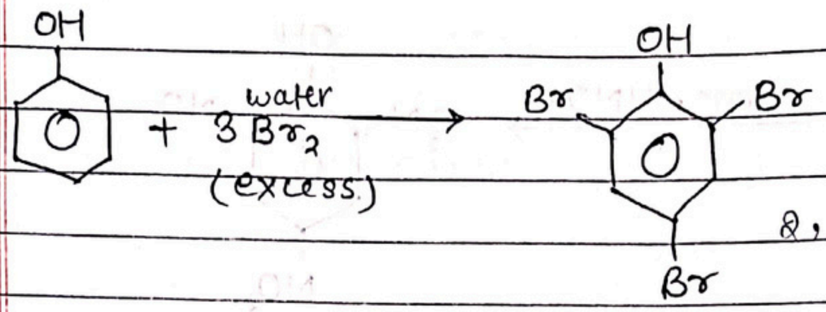
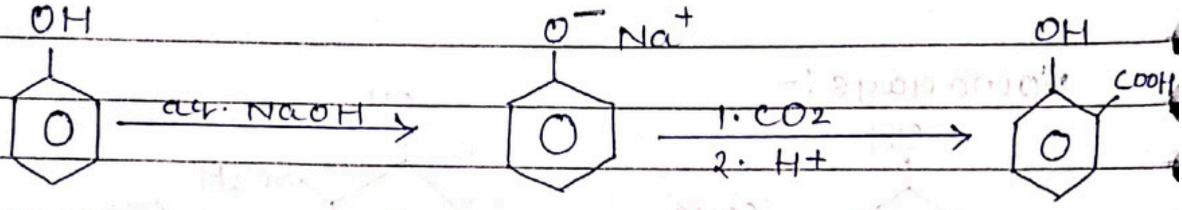


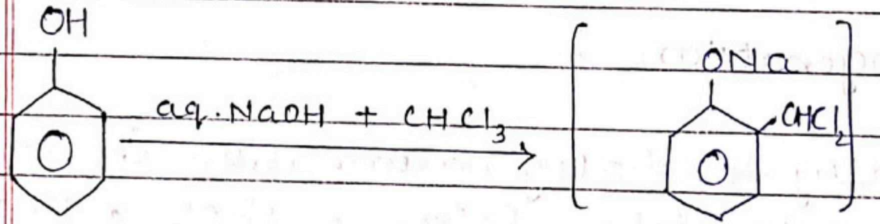
2,4,6-Tribromophenol

(c)* KOLBE'S REACTION :-



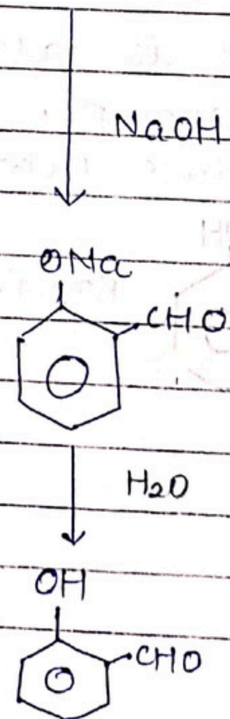
Phenol. Sodium phenoxide Salicylic acid (major)

(d)* Reimer Tiemann Reaction:



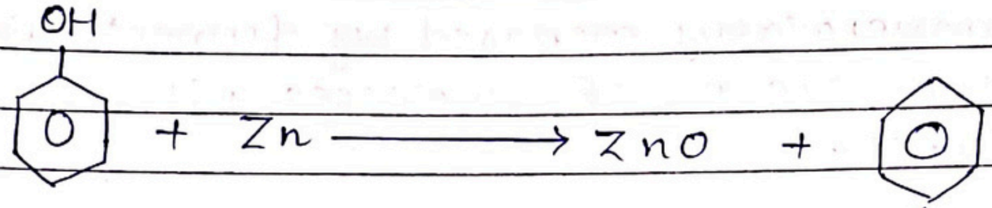
Intermediate

$\ddot{C}Cl_2$ dichlorocarbene



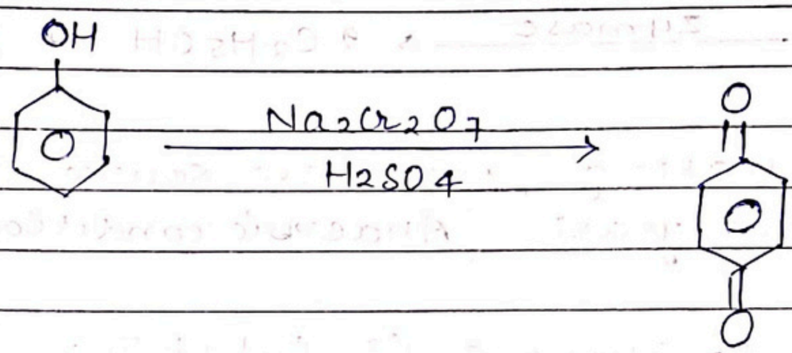
(salicaldehyde)

(e) Reaction with zinc dust :



benzene.

(f) Oxidation :



Benzoquinone.

Some commercially Important Alcohols :-

1). Methanol : CH_3OH : WOOD SPIRIT (destructive distillation of wood.)

$$\underset{\text{(syngas)}}{CO + 2H_2} \xrightarrow[\substack{200-300 \text{ atm} \\ 573-673 \text{ K}}]{ZnO - Cr_2O_3} CH_3OH$$

↳ colourless liquid
↳ B.P - 337 K
↳ Poisonous
↳ Ingestion of even small quantity cause blindness and even death (in large q.).
↳ used as solvents in paints , varnishes and formaldehyde.

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2. Ethanol : C_2H_5OH

1 Commercially prepared by fermentation from sugar of molasses, sugarcane, grapes.

$$\underset{\text{sugar. sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

In wine making grapes are source of sugar and yeast [Anaerobic condition].

The action of zymase is inhibited once the % of alcohol excess 14 percent.

(If air enters the fermented mix, it destroys the taste of ethanol by converting into CH_3COOH.

* ethene $\xrightarrow{\text{hydration}}$ ethanal.

↳ colourless
↳ B.P 351 K
↳ solvent
↳ preparation of carbon compound.

* Denaturation of alcohol :
The commercially alcohol is made unfit for drinking by mixing in it some copper sulphate (give it colour) and pyridine (a foul smelling liquid).

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Ethers :-

Methods of Preparation :-

1. By dehydration of alcohols :-

↳ Alcohols undergo dehydration in the presence of PROTIC ACIDS like H_2SO_4, H_3PO_4 etc.

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

$$CH_3-CH_2-OH \xrightarrow[413K]{H_2SO_4} C_2H_5OC_2H_5 \ (1° \text{ and symm.})$$

↓ in this reaction 2° or 3° ethers are not obtained. as it follows S_N2 pathway. and more alkyl group caus S.H

Mechanism :-

$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^{\oplus} \longrightarrow CH_3-CH_2-\overset{\oplus}{O}(H)-H$$

$$\downarrow$$

$$CH_3-\overset{\oplus}{C}H_2 + H_2O$$

S_N2 pathway

$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + CH_3-\overset{\oplus}{C}H_2 \longrightarrow CH_3-CH_2-\overset{\oplus}{\underset{|\atop H}{O}}-CH_2-CH_3$$

$$CH_3-CH_2-\overset{\oplus}{\underset{|\atop H}{O}}-CH_2-CH_3 \longrightarrow CH_3-CH_2-\ddot{\underset{..}{O}}-CH_2-CH_3 + H^{\oplus}$$

* if 2°/3° alcohal then rxn will enter in elimination pathway because of bulky :Nu: → produced Alkene

2. Williamson Synthesis :-

↳ This reaction helps to prepare both symme and unsymmetrical ethers.

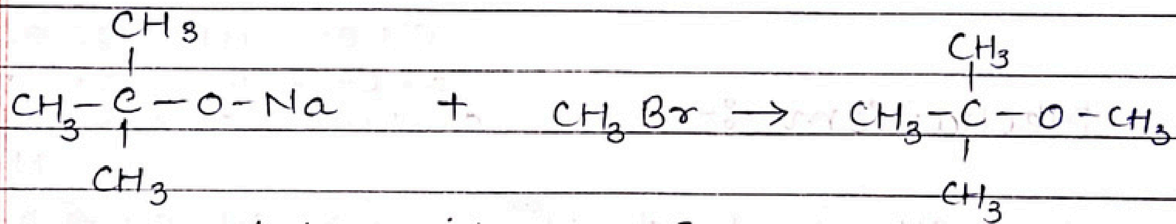
↳ 1°, 2° and 3° are also prepared.

↳ This reaction follows S_N2 pathway, where alkoxide ($:Nu^{\ominus}$) attacks 1° alkyl halide. (1°/2°/3°)

↳ Alkyl halide should be 1° and alkoxide can 1°/2°/3°.

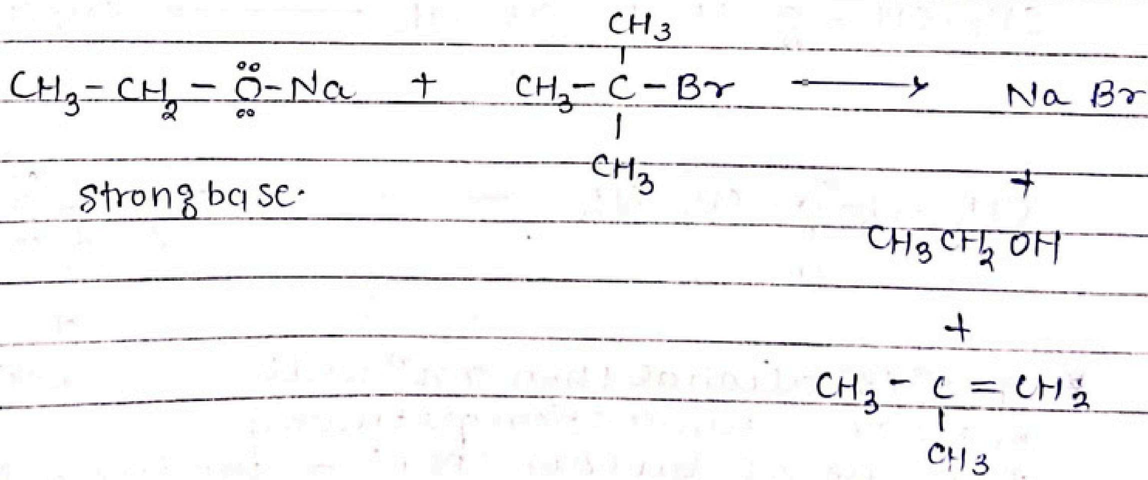
$$R-\ddot{\underset{\cdot\cdot}{O}}-Na \; + \; RX \; \rightarrow \; NaX \; + \; R-O-R'$$

sodium alkoxide.



sodium t-butoxide. 2methoxy-2-methylpropane + NaBr.

↳ Better result are obtained if alkyl halide is primary.

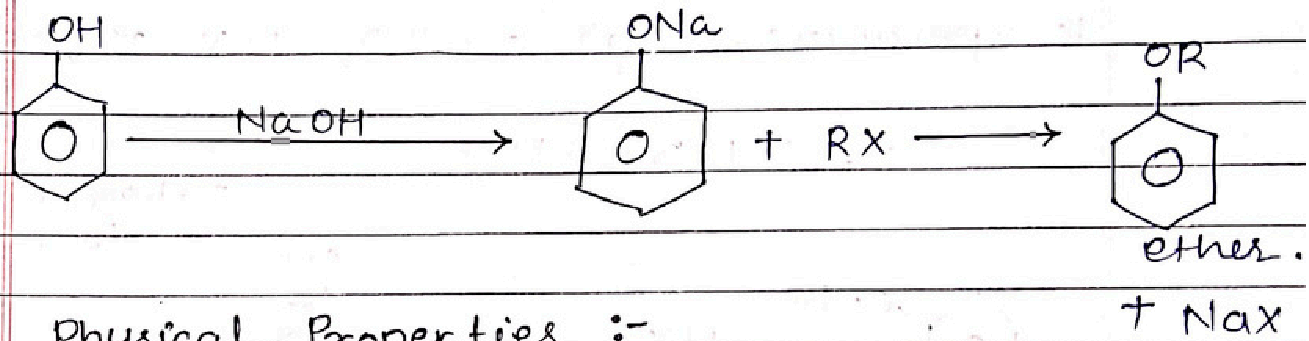


strong base.

Alkoxide are strong base.

↳ Alkyl halide are 2°/3° type then because of steric hinderance alkoxide will not be able to attack these alkyl halides.

↳ Alkoxide being basic nature will accept β-hydrogen and ∴ Alkenes will form. [β-elimination Pathway]



Physical Properties :-

1). An ether molecule has a net dipole moment due to the polarity of C–O bonds.

2). the boiling point of ether is comparable to alkanes but much lower than that of alcohols of comparable molecular mass despite the polarity of the C-O bond. the miscibility of ethers with water resembles those of alcohols.

3). Ether molecules are miscible in water. this is attributed to the fact that like alcohol, the oxygen atom of ether can also form hydrogen bonds with a water molecule.

Chemical Reactions :-

(I). Cleavage of C-O bond in Ethers :

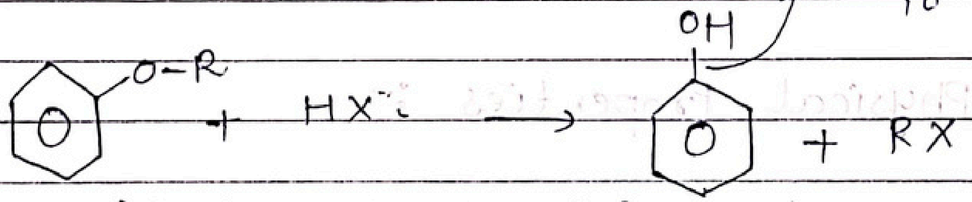
$R-O-R + HX \rightarrow R-O-H + RX$
alcohol   alkyl halide

$R-OH + HX \rightarrow RX + H_2O$.

↳ C-O bond is difficult to break, extreme conditions are required like like high temperature, high conc^n of HX required.

$HI > HBr > HCl$

OH bond is difficult to break.



↳ Reaction will stop after phenol formation.

$CH_3-O-CH_3 + HI \longrightarrow CH_3OH + CH_3I$

$CH_3OH + HI \longrightarrow CH_3I + H_2O$

↳ in case of unsymmetrical ether,

(First Product)

$CH_3-O-CH_2CH_3 + HI \rightarrow CH_3CH_2I$ or CH_3I ? ✓

Reason: we will get CH_3I because the reaction follows S_N2 pathway and hence $I^{\ominus}$ ($:Nu^{\ominus}$) will attack the C with least steric hinderance.

Acidity $\propto$ anion

$\propto -I \quad \propto -M$

$\propto \frac{1}{+I} \quad \propto \frac{1}{+M}$

Mechanism :

Step I, $\;H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-CH_3 + HI \longrightarrow \left[I\cdots \underset{H\;\;H}{\overset{H}{C}} \cdots \underset{H}{\ddot{O}^{\oplus}}-CH_2CH_3 \right] \longrightarrow CH_3I + CH_3CH_2OH$

Step (II) $\;CH_3-\underset{H}{\overset{H}{C}}-\ddot{\underset{..}{O}}-H + HI \longrightarrow \left[I\cdots \underset{CH_3}{\overset{H\;\;H}{C}} \cdots \underset{H}{\ddot{O}^{\oplus}}-H \right] \longrightarrow CH_3CH_2I + H_2O$

Note: This mechanism is valid when 1°/methyl group present in ether.
But if ether contain 2°/3° groups, it will enter in S_N1 mechanism.

Step (I) $\;CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\ddot{\underset{..}{O}}-CH_3 + \overset{+\delta}{H}\overset{\delta-}{I} \xrightarrow[\text{(slow)}]{S_N1} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\ddot{O}^{\oplus}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}{}^{\oplus} + CH_3OH$

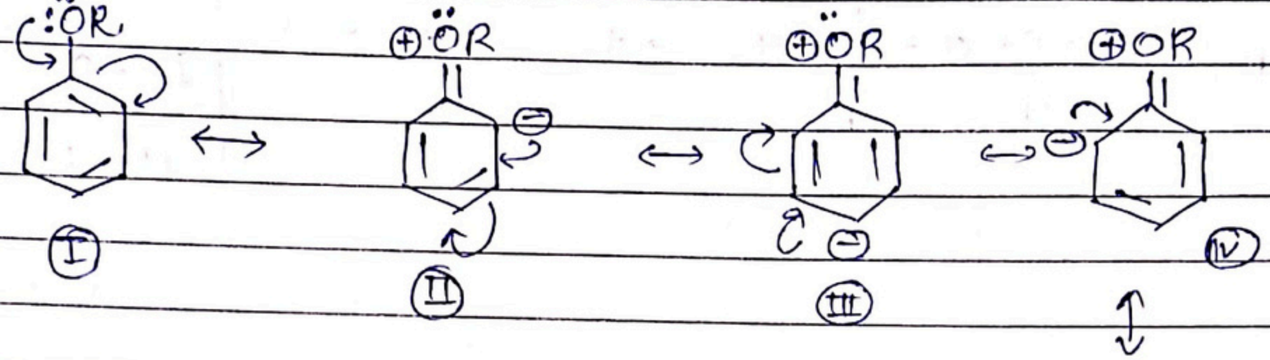
Step (II) $\;CH_3-\underset{CH_3}{\overset{CH_3}{C}}{}^{\oplus} + I^- \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$

(1st)

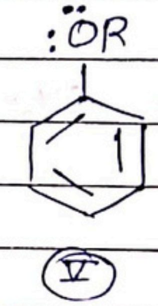
Step (III) $\;CH_3OH + HI \longrightarrow CH_3I + H_2O.$

(2nd)

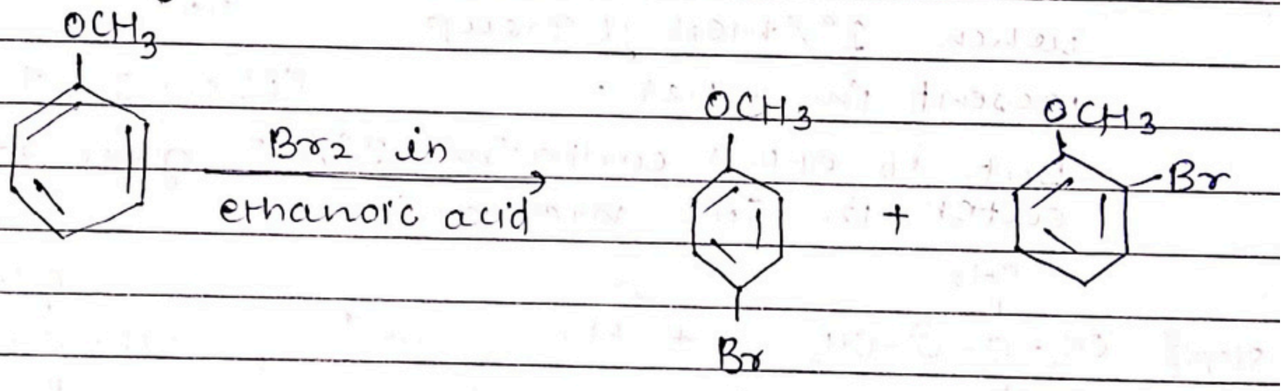
2. Electrophilic Substitution Reaction :



-ve charge desity increases on o and p position.
∴ $E^{\oplus}$ attack on o and p position.

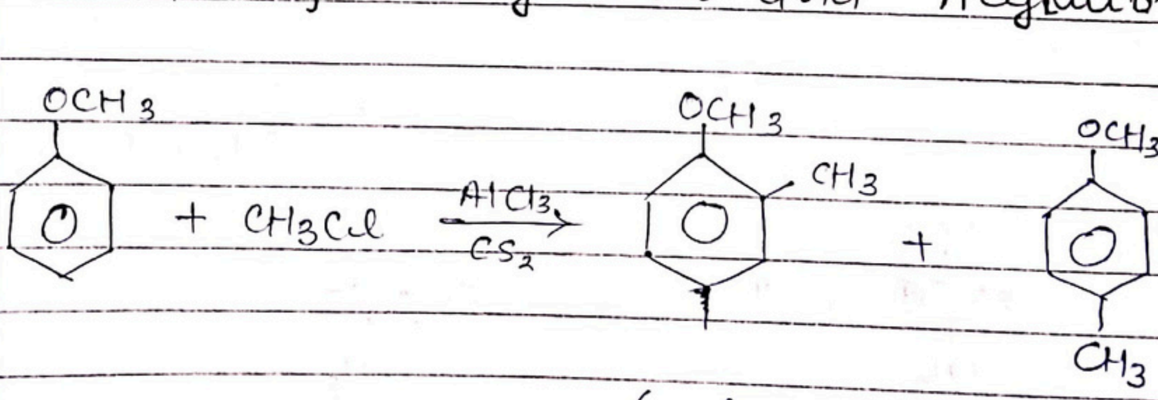


i) Halogenation :

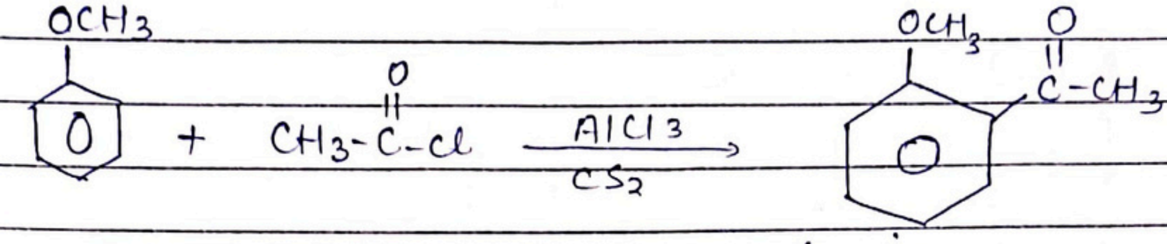


(major) (minor).

ii) Fridel craft Alkylation and Acylation :

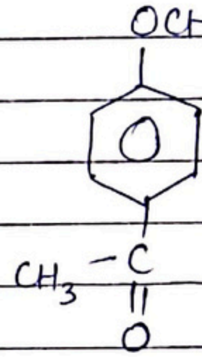


(minor) (major)



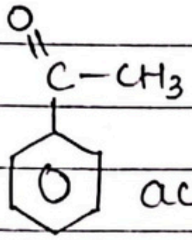
(minor)

+



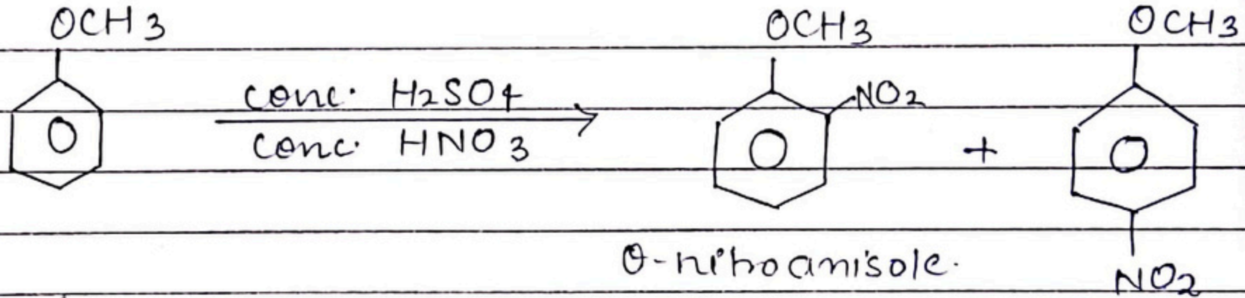
(major)

4-methoxy acetophen-one.



acetophenone.

(iii) Nitration :



O-nitroanisole. (minor)

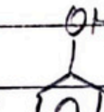
p-nitro Anisole (major)

(I_2/NaOH)

Iodoform test (yellow ppt).

[which gives] one $CH_3-CH(OH)-$

$FeCl_3$ test (which one gives)

6  + $FeCl_3$ ⟶ $[Fe(C_6H_5O)_6]^{3-}$ + $3H^+$ + $3HCl$

violet colour