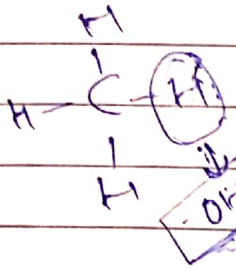
Unit - II

Alkohols, phenol, and Ethers.

① Introduction.



CH_4 – Methane [Hydrocarbon]

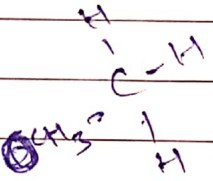
CH_3OH → Methanol [Alcohol]

↳ Hydroxy group.

→ phenol.

C_6H_5OH.

C_6H_6 → C_6H_5OH → phenol.



CH_3OCH_3 – dimethyl ether.

↳ Alkoxy group

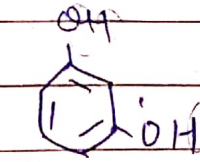
Classification:

[a] Alcohol and phenols

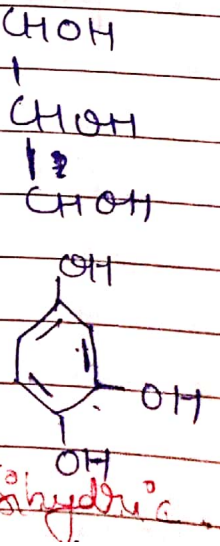
↳ They are Classified as, Mono, Di, Tri or polyhydric

Ex: CH_2H_5OH

Monohydric



Dihydric



Trihydric

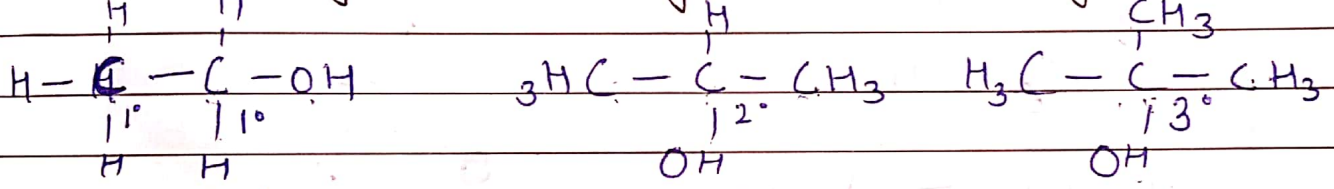
→ Monohydric alcohol further classified to hybridisation of Carbon atom to which hydroxy group is attached.

(i) Compound Containing $Sp^3 - OH$ bond.

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

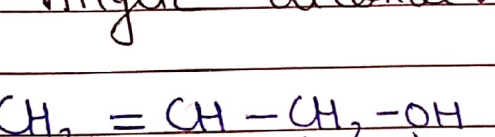
→ They are further classified as.

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

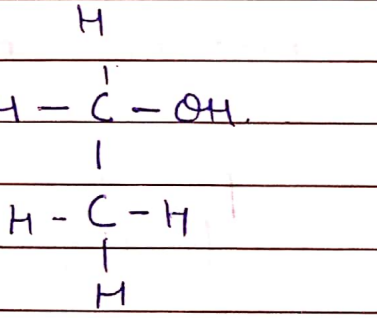


primary (1°) Secondary (2°) Tertiary (3°)

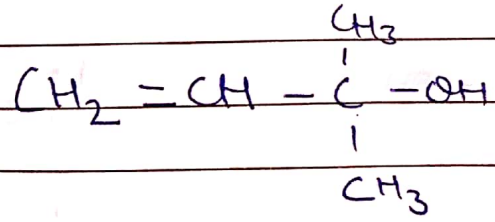
[b] Allylic alcohol.



primary



Secondary



Tertiary.

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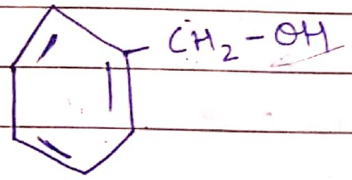
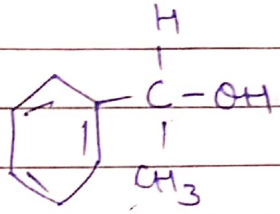
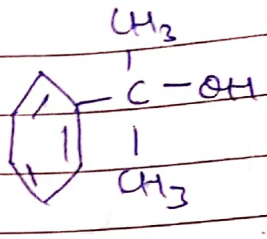
[c] Benzylic alcohol.



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) $C_2H_5OCH_3$ → Unsymmetrical.

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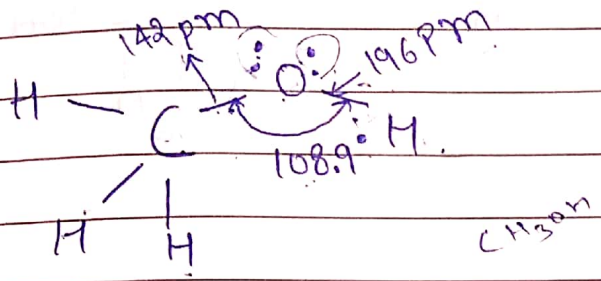
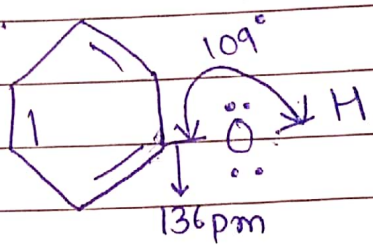
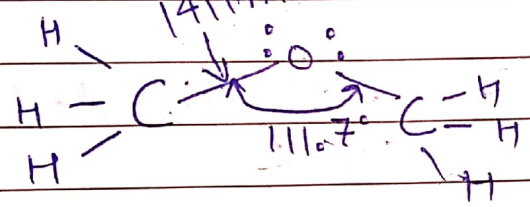
Structure of functional group.



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 methanol. 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.

⊙ $>C=C< + H_2O \xrightarrow{H^+} >C(H)-C(OH)<$

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

→ Mechanism

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

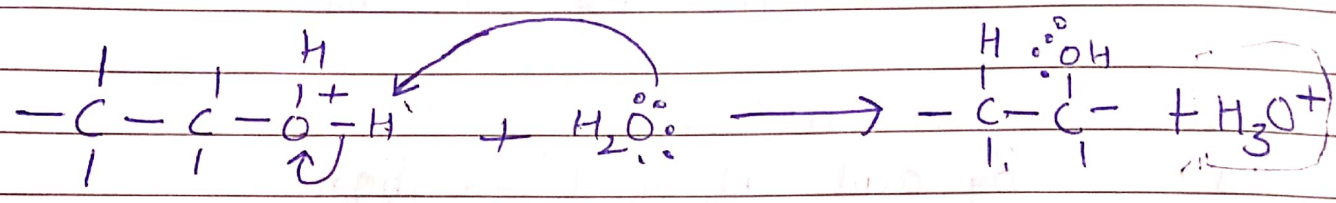
$$H_2O + H^+ \longrightarrow H_3O^+$$

$$>C=C< + H-\ddot{O}(H)-H \longrightarrow -C(H)-C^+< + H_2\ddot{O}:$$

STEP-2: Nucleophillic attack of water on Carbocation.

$$-C(H)-C^+< + H_2\ddot{O}: \longrightarrow -C(H)-C(H)-\overset{+}{O}(H)-H$$

STEP-3 Deprotonation to form an alcohol.



(ii) From By hydroboration Oxidation.

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

$$\downarrow CH_2-CH=CH_2$$

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

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

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

Propane-1-ol.

(i) $3CH_3-CH=CH_2 \xrightarrow[H_2O_2]{B_2H_6} 3CH_3-CH_2-\overset{\ominus}{C}H_2-OH + B(OH)_3$

OH^-

2. from Carbonyl Compounds.

[i] Reduction of aldehyde and ketone.

- $RCHO + H_2 \xrightarrow{Pd} RCH_2OH$
- $RCOR' \xrightarrow{NaBH_4} R-\underset{\underset{OH}{|}}{CH}-R'$

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.

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

Adduct

$$>\underset{\underset{R}{|}}{C}-OH + Mg(OH)X \leftarrow H_2O$$

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① $H_2C=O$ + $RMgX \rightarrow RCH_2OMgX$

Methanal.

$\xrightarrow{H_2O}$ $RCH_2OH + Mg(OH)X$

1° alcohol.

② $R_2C=O$ + $R'MgX \longrightarrow R-CH(R')-OMgX$

$\xrightarrow{H_2O}$ $R-CH(R')-OH + Mg(OH)X$

2° alcohol.

③ $R_2C=O$ + $R'MgX \longrightarrow R-C(R')(R)-OMgX$

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

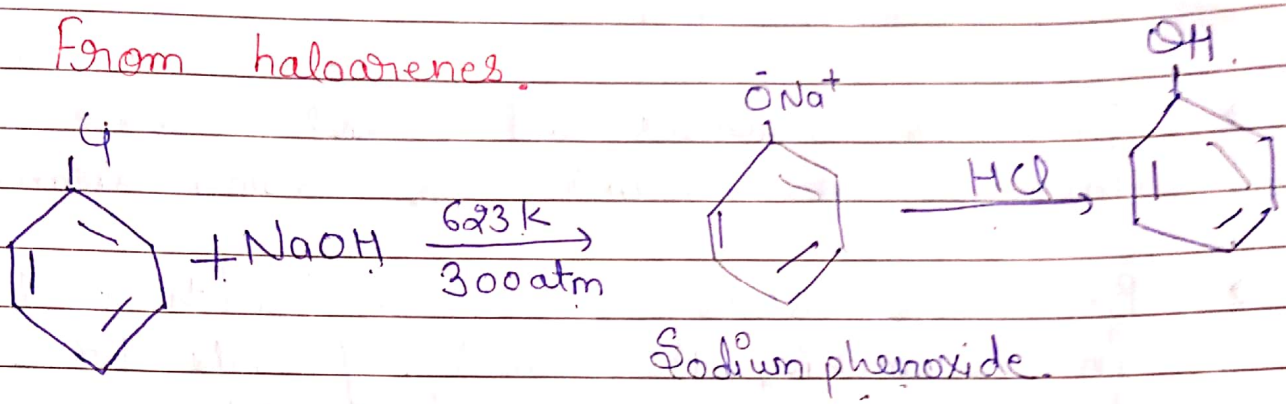
3°

NOTE

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

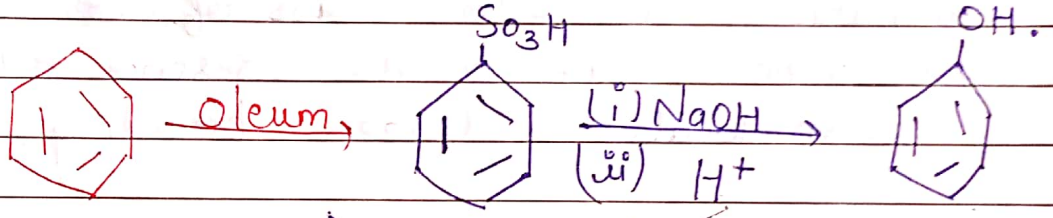
Preparation of phenol.

1 From haloarenes.



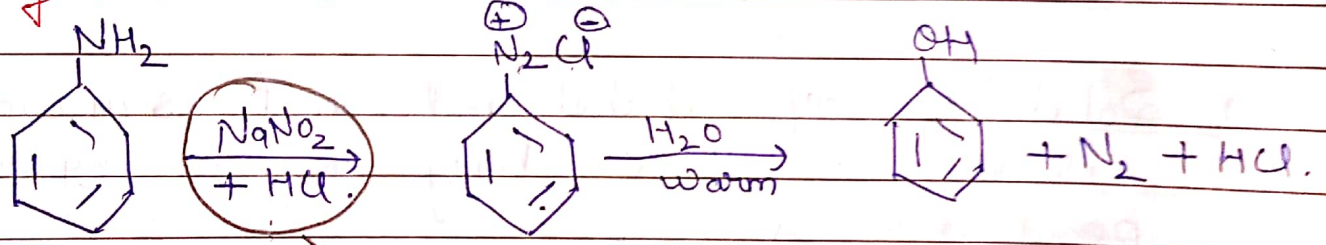
Sodium phenoxide.

2 from benzenesulphonic acid.



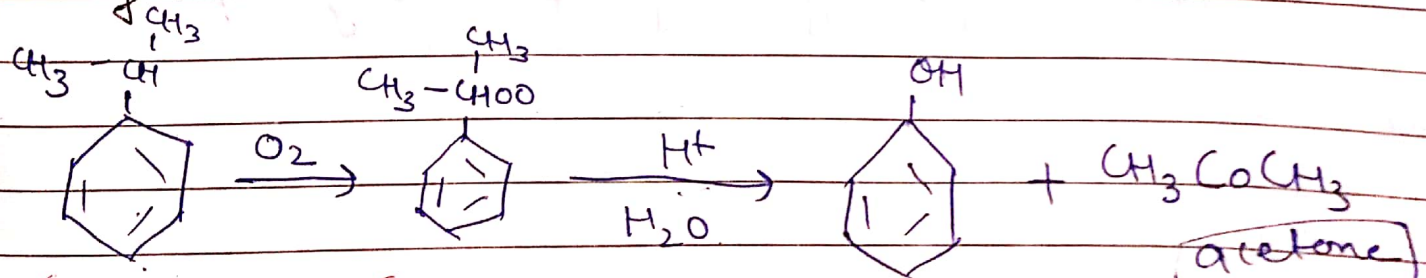
Benzene Solphonic acid.

3. from diazonium Salt



Aniline. Nitrous acid

4. from Cumene.



Cumene. Cumene hydroperoxide. Phenol. acetone ↓ large amount.

Physical properties.

① 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.

⇒

② Solubility.

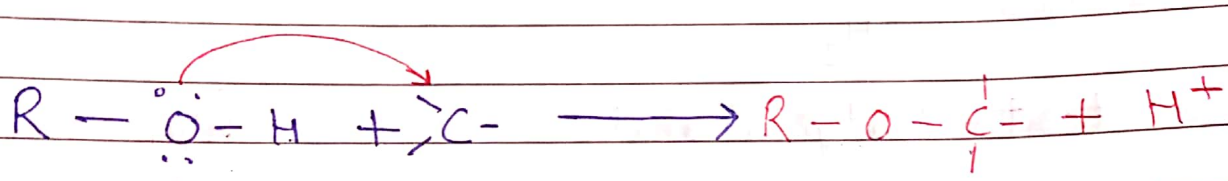
→ Solubility of alcohol and phenol is in water is due to their ability to form hydrogen bond with Water.

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

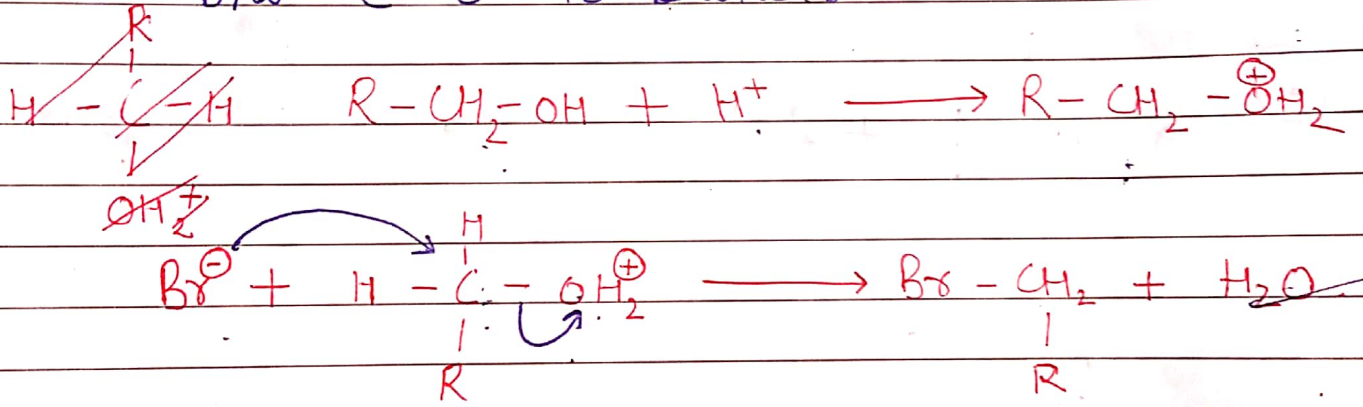
CHEMICAL REACTIONS.

- 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.



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



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

1. Acidity of alcohols and phenols.

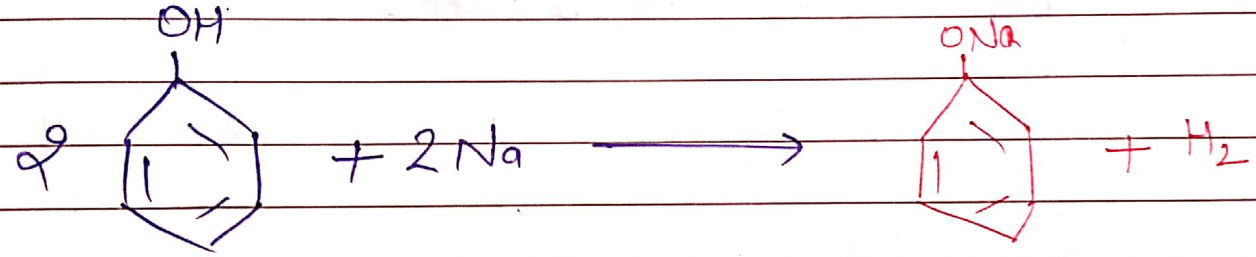
→ Alcohol and phenol react with Metal Such as Sodium, potassium and aluminium to yield alkoxide/phenoxide.

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

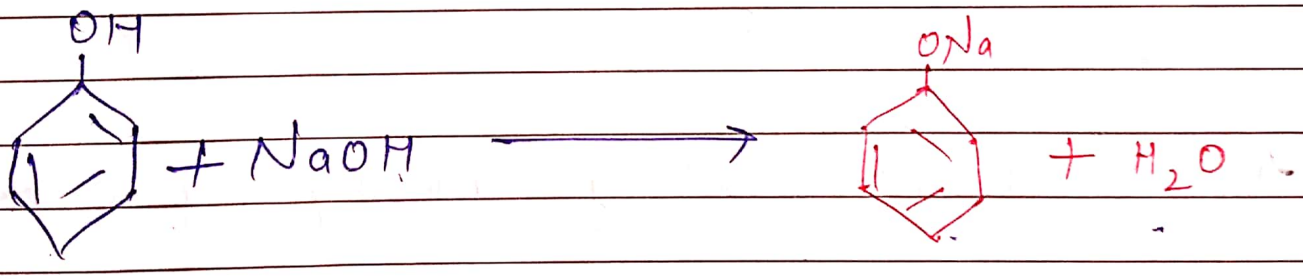
Sodium alkoxide.

⊙ $6\,(CH_3)_3C-OH + 2Al \longrightarrow 2\left[(CH_3)_3C-O\right]_3Al + 3H_2$

tert-Butyl alcohol. Aluminium tert-butoxide

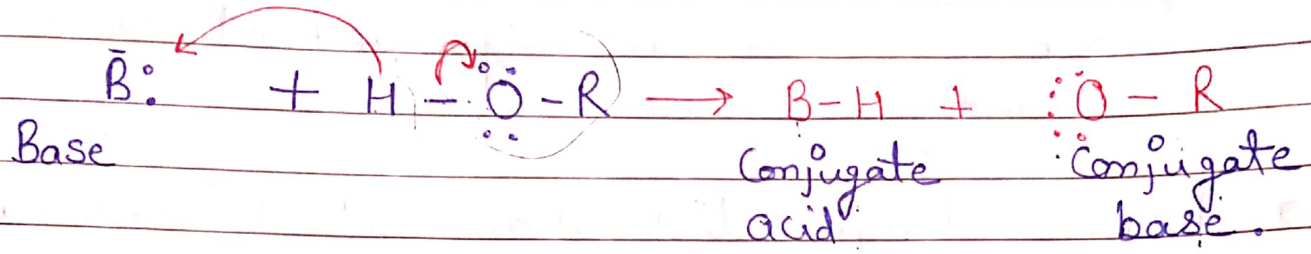
⊙ 

Sodium phenoxide.

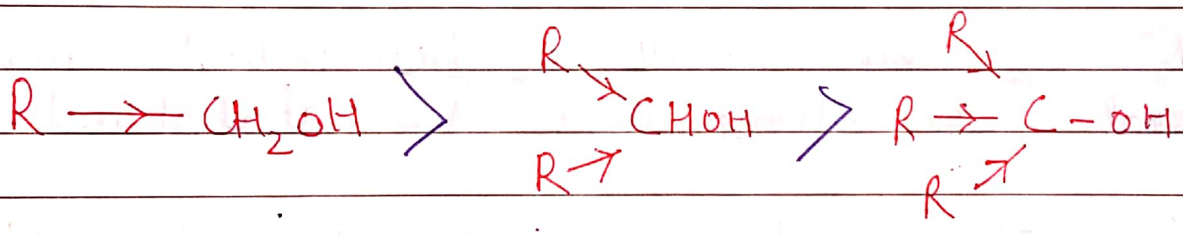
⊙ 

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

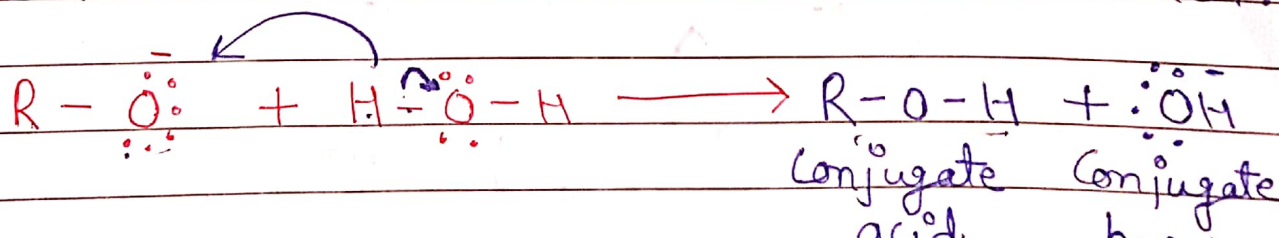
⊙ Alcohol and phenol are Bronsted acid. i.e they can donate a proton to a strong base.



[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.



→ Alcohols are weaker acid than water.

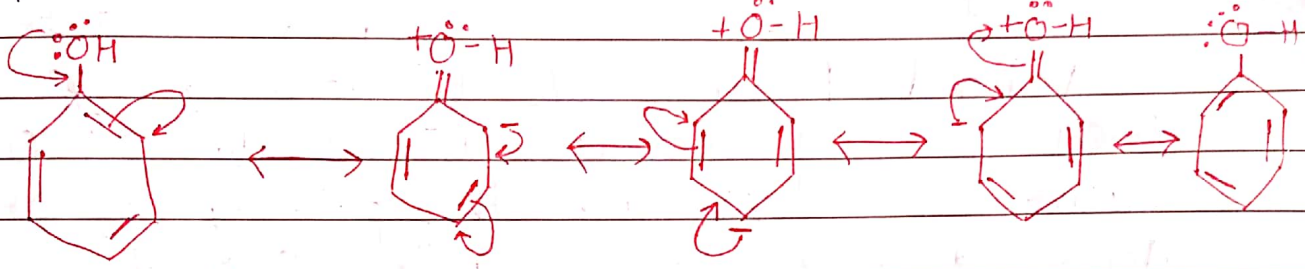


⊙ Alcohol act as Bronstead base as well due to the presence of unshaired paired e^- on oxygen. which make them proton acceptor.

(iii) Acidity of phenols :

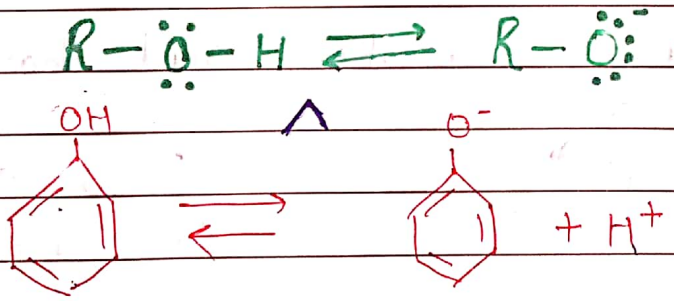
⊙ Hydroxy group is directly attached to Sp^2 hybridised Carbon of benzene ring and act as e^- withdrawing group.

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



→ The R^n 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 :



Due to higher electronegativity of Sp^2 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~~

alcahal.

→ 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.

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

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

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

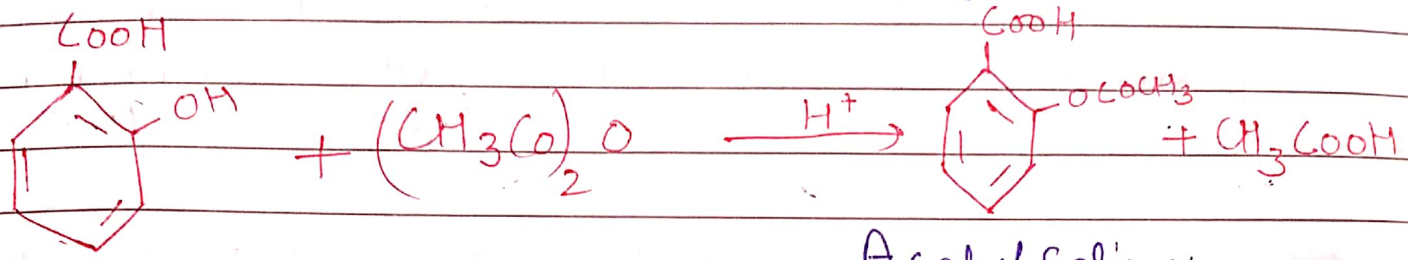
⊙ $Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$

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

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

⊙ 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:

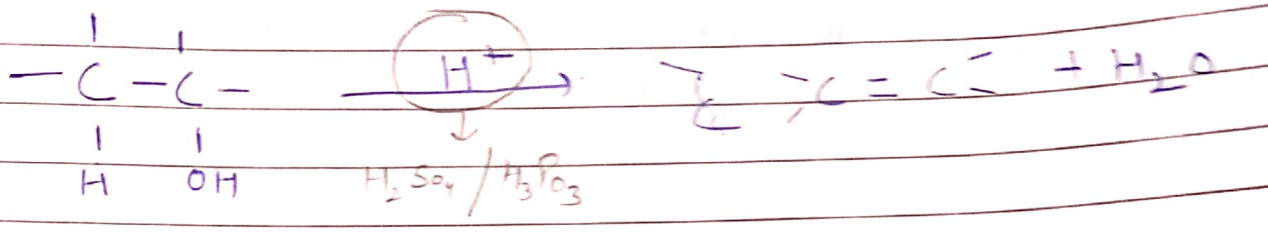
$$ROH + HX \longrightarrow R-X + H_2O$$

→ 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]

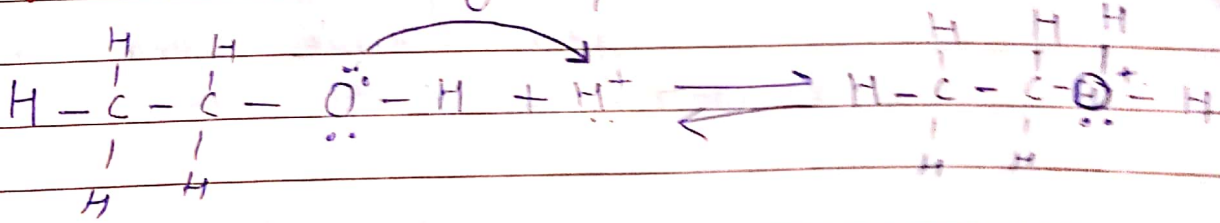


- $C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2=CH_2 + H_2O$
- $CH_3-\underset{2^\circ}{\overset{OH}{\underset{|}{CH}}}-CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_3} CH_3-CH=CH_2 + H_2O$
- $CH_3-\overset{CH_3}{\underset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\underset{||}{C}}-CH_3 + H_2O$

Tertiary > Secondary > Primary

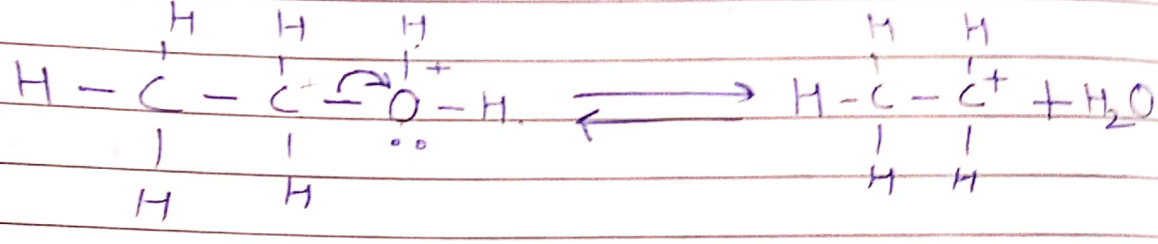
→ Mechanism

① STEP 1: Formation of protonated alcohol.

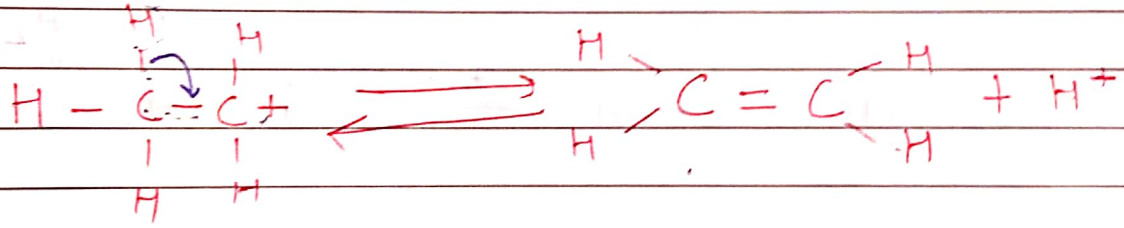


Protonated alcohol
(Ethyl Oxonium Ion)

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



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



⊙ 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.

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

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

acidic $KMnO_4$

⊙ $RCH_2OH \xrightarrow{CrO_3} RCHO$

⊙ $CH_3-CH=CH-CH_2OH \xrightarrow[\downarrow]{PCC} CH_3-CH=CH-CHO$

Pyridinium chlorochromate

⊙

$$R-\underset{\underset{OH}{|}}{\overset{\overset{1^\circ}{|}}{CH}}-R' \xrightarrow{CrO_3} R-\underset{\underset{O}{||}}{C}-R'$$

NOTE: 3° Alcohol do not Undergo oxidation.

⊙ When Vapour of 1° or a 2° alcohol are passed over heated Cu at 573 k. then.

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

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

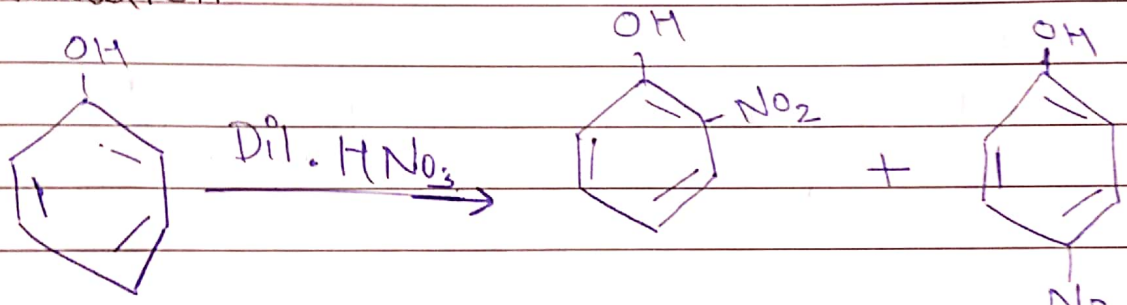
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[573k]{Cu} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Reactions of Phenols

1. Electrophilic aromatic Substitution.

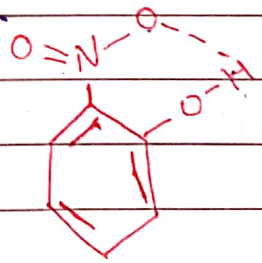
- The -OH group attached to benzene ring activates it toward electrophilic Substitution.
- Also it direct the incoming group to ortho and para possition in ring as these position become electric rich due to resonance effect caused by -OH group

[i] Nitration

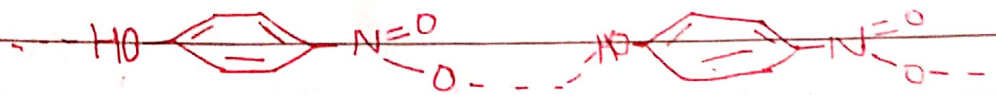


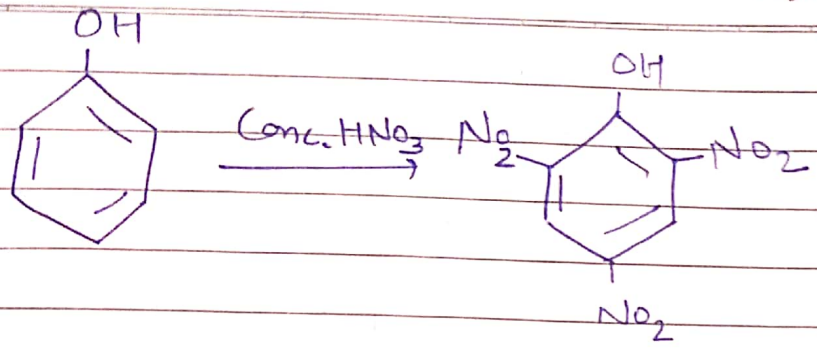
O-Nitrophenol p-Nitrophenol.

→ 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

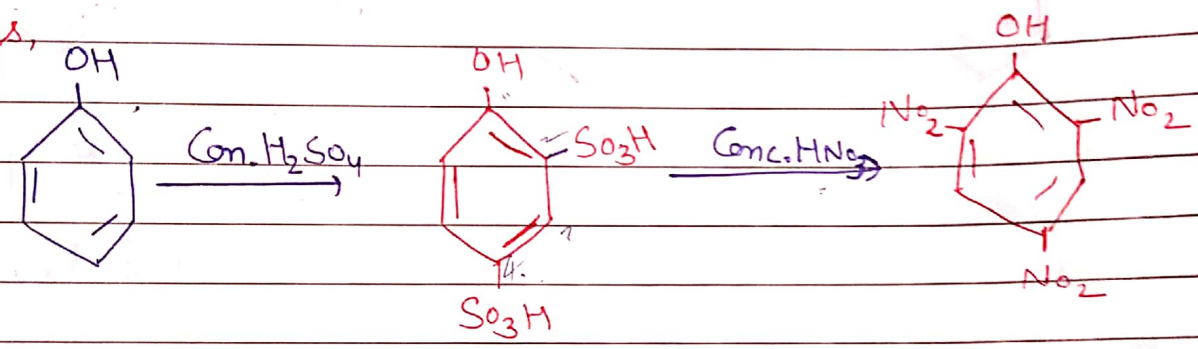




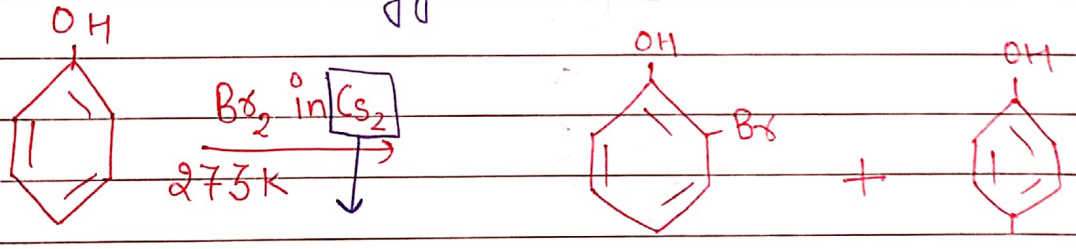
2,4,6 - Trinitrophenol.
(picric acid)

The yield of reaction product is poor.

Nowdays,



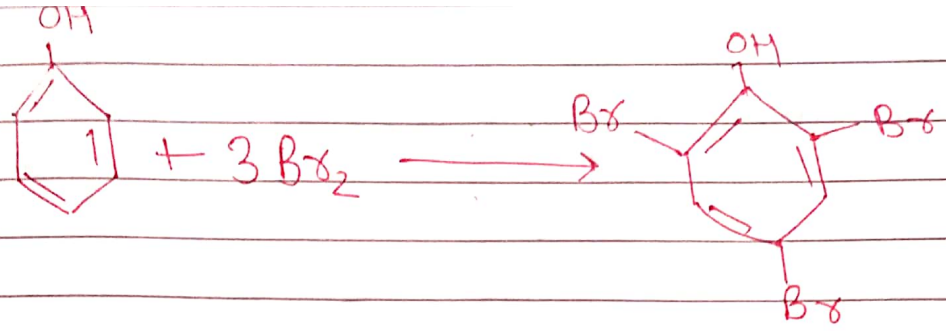
[ii] Halogenations: Treating phenol with bromine different product are formed under different condition.



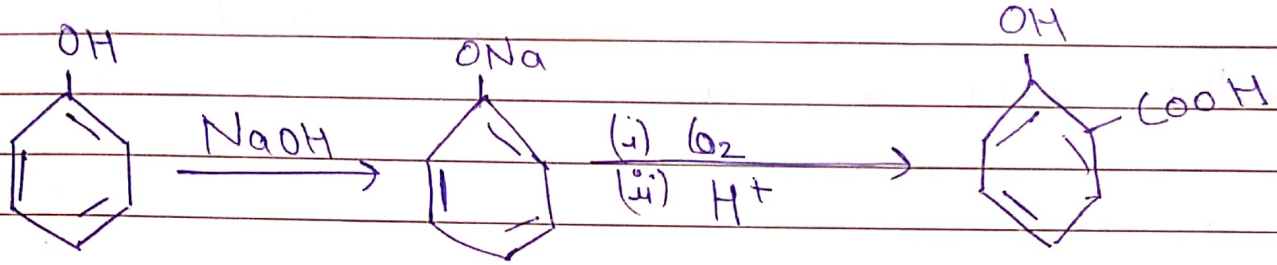
Solvent of low polarity.

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.



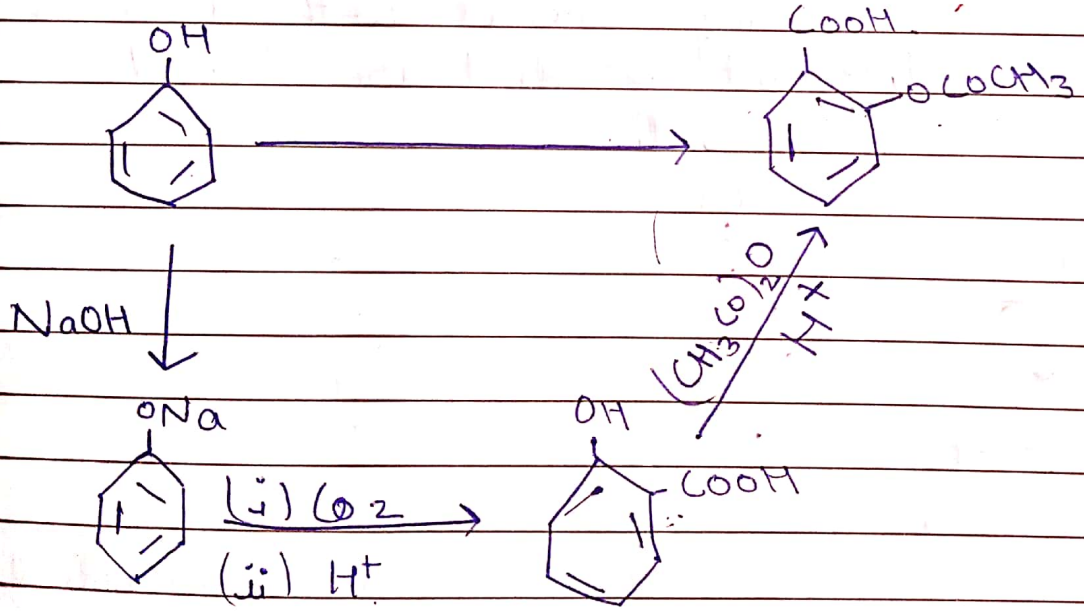
2. Kolbe's reaction



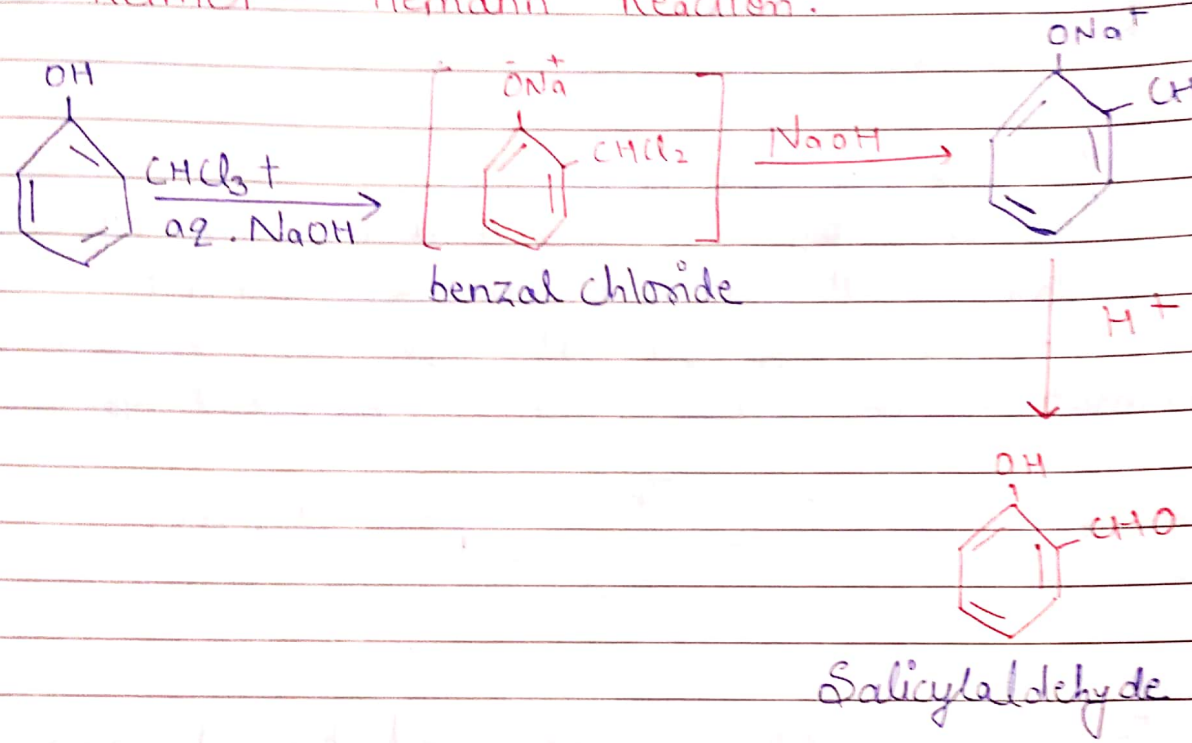
2-Hydroxybenzoic acid

(Salicylic acid)

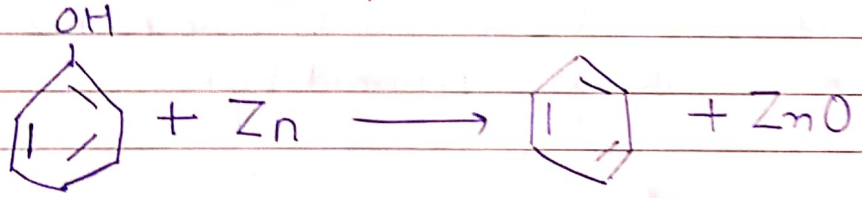
Q. Convert phenol into Aspirin.



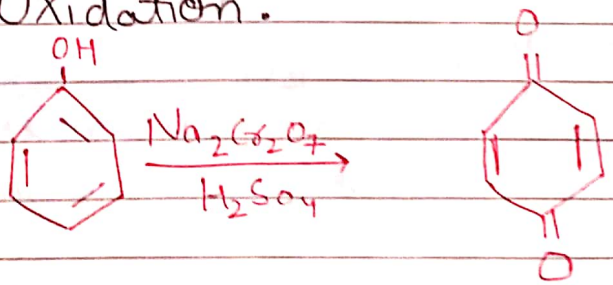
3. Reimer - Tiemann Reaction.



4. Reaction of phenol with Zinc dust.



5. Oxidation.



benzoquinone.

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

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

→ It is a Colourless liquid and boil at 337K.
→ 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 351K. used as Solvent in paint industury. Commercially alcohol made Unfit for drinking by adding $CuSO_4$ and pyridine. It is known as denaturation of alcohal.

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ETHERS

Preparation of ether

1. by dehydration of alcohol.

→ Alcohols undergo dehydration in presence of protic acid (H_2SO_4, H_3PO_4). Reaction product depend on reaction condition.

CH_3CH_2OH —(H_2SO_4, 443 K)→ $CH_2=CH_2$ (ethene)

CH_3CH_2OH —(H_2SO_4, 413 K)→ $C_2H_5OC_2H_5$ (ethoxy ethane)

⊙ Formation of ether is (S_N2) reaction involving the attack of alcohol on a protonated alcohol.

[i] $CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{O}(H)-H$

[ii] $CH_3CH_2-\ddot{O}(H)\!: + CH_3-CH_2-\overset{+}{O}(H)-H \longrightarrow CH_3CH_2-\overset{+}{O}(H)-CH_2CH_3 + H_2O$

[iii] $CH_3CH_2-\overset{+}{O}(H)-CH_2CH_5 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

ether

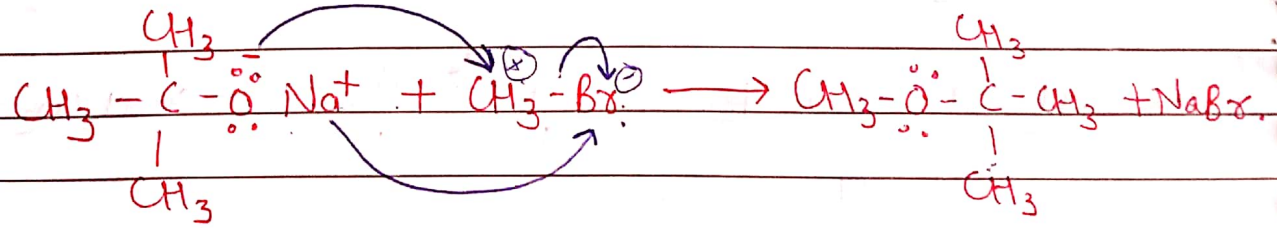
- The method is suitable for preparation of ethers having primary alkyl groups only.
- The reaction follow S_N1 pathway when the alcohol 2° or 3°.
- dehydration of secondary and tertiary alcohols to give ethers is unsuccesful. and alkenes are easily formed.

2. Williamson Synthesis

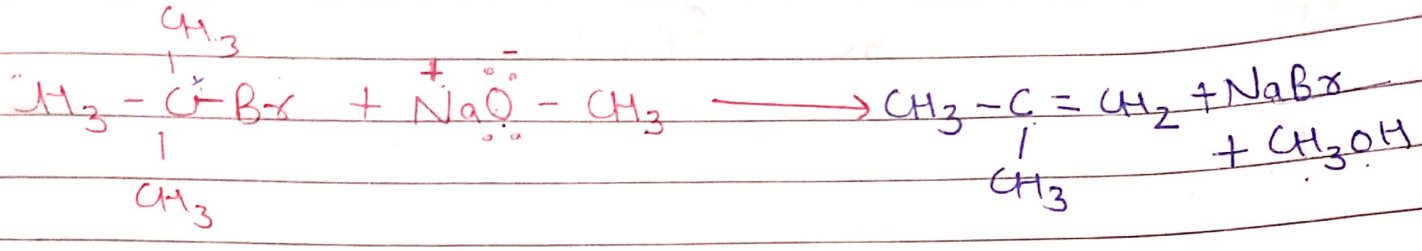
- In this method an alkyl halide is allowed to react with Sodium alkoxide.

$$R-X + R'-\ddot{O}:Na^+ \longrightarrow R-\ddot{O}-R' + NaX$$

- Ethers containing substituted alkyl group (3° or 2°) also prepared by this method.

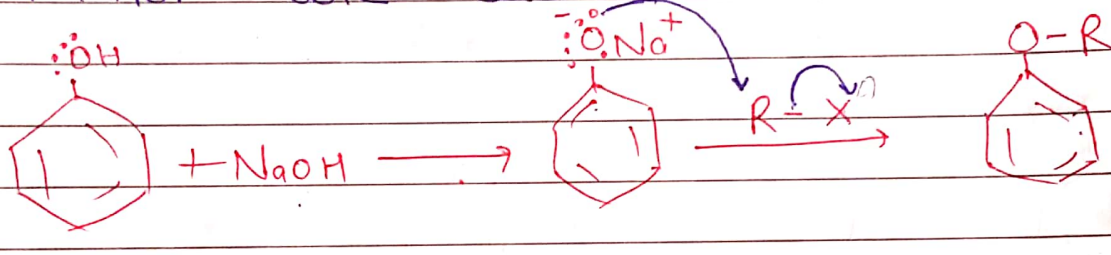


- Better result are obtained if alkyl halide is primary In case of 2° or 3° alkyl halide elimination competes over substitution



→ It is because alkoxide are also strong base as well. They react with alkyl halide leading to elimination R^n.

⊙ Phenol are also converted into ether.



Physical properties

⊙ B.P of ethers are comparable of alkene having comparable molecular mass. but less than that of alcahol.

⊙ The miscibility of ether with water resembleless those of alcahol of same molecular mass. due to the presence of Oxygen in ether. which can also form hydrogen bonding with water.

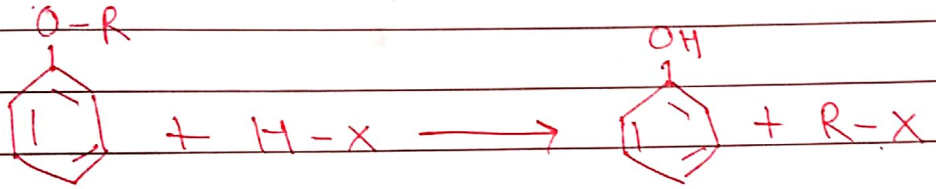
CHEMICAL REACTION.

1. Cleavage of C-O bond in ethers.

Reaction of dialkyl ~~ether~~ ether give two molecules alkyl halide when react with excess of hydrogen halide.

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

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

① 

② $R-O-R' + HX \longrightarrow R-X + R'-OH$

③ order of reactivity of hydrogen halide.

$$HI > HBr > HCl$$

→ Cleavage of ether take place with Conc. HI or HBr at high temprature.

④ Mechanism

1. $CH_3-\ddot{O}-CH_2CH_3 + H-I \rightleftharpoons CH_3-\overset{H}{\overset{\oplus}{O}}-CH_2CH_3 + I^-$

2. $I^- + CH_3-\overset{H}{\overset{\oplus}{O}}-CH_2CH_3 \longrightarrow \left[I--CH_3-\overset{H}{\overset{\oplus}{O}}-CH_2CH_3\right] \longrightarrow CH_3-I + CH_3CH_2-OH$

3. $CH_3CH_2-\ddot{O}-H + H-I \rightleftharpoons CH_3CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}H + I^-$

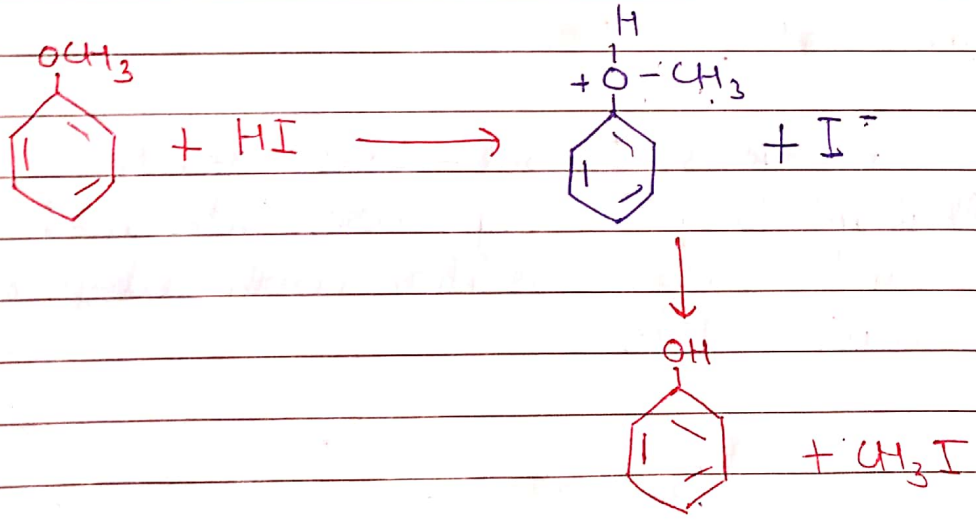
$I^- + CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow CH_3CH_2I + H_2O$

(c) $CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)_2-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)_2-I$

Mechanism.

$CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)_2-\overset{+}{\underset{H}{O}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\overset{+}{C}}}(CH_3)_2 + CH_3OH$

$CH_3-\overset{CH_3}{\overset{|}{\overset{+}{C}}}(CH_3)_2 + I^- \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)_2-I$

(d) 

→ The bond blw $O-CH_3$ is weaker the the bond blw $O-C_6H_5$ because carbon of phenyl group is Sp^2 hybridised and there is a partial double bond character.

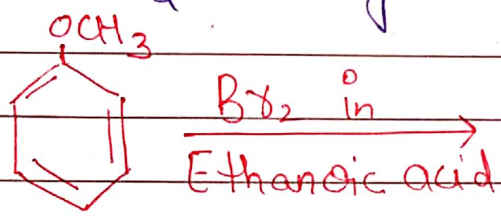
2. Electrophilic Substitution.

⊙ The alkoxy group (-OR) is Ortho and para directing.

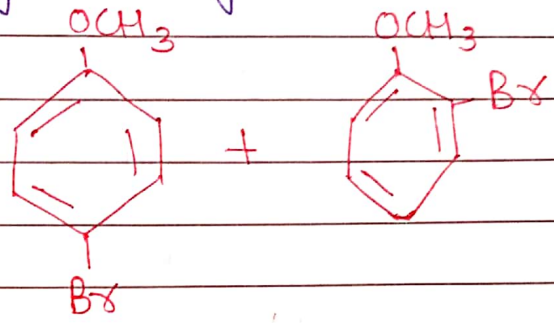
[i] Halogenation :

⊙ phenylalkyl ethers undergo halogenation in benzene ring.

eg.



Anisole

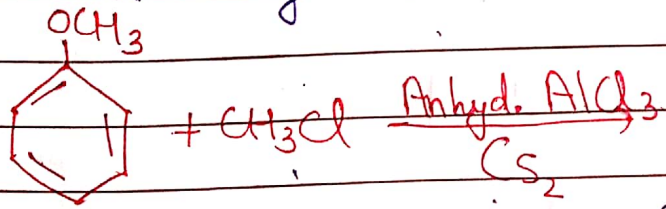


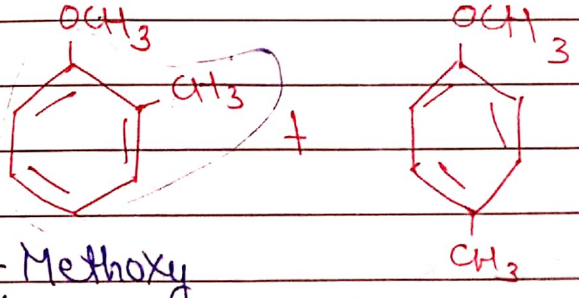
90% 10%.

p-Bromoanisole

[ii] Friedal Craft reaction :

⊙ Anisole undergoes friedal-Craft reaction i.e alkyl and acyl group are introduced at Ortho and para possition. With alkyl halide and acyl halide.





2-Methoxy toluene

4-methoxy toluene.

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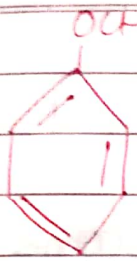
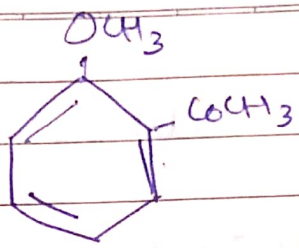


+ CH_3COCl

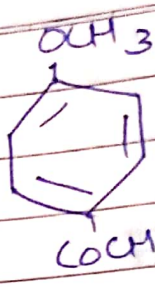
Ethanoyl Chloride

$\xrightarrow{\text{Anhyd. } AlCl_3}$



2-Methoxy acetophenone

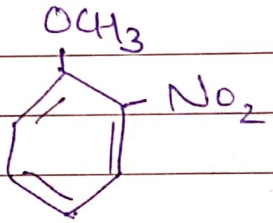
+



4-methoxy acetophenone

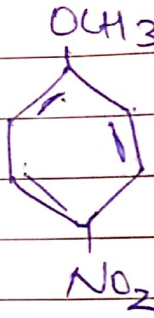
[iii] Nitration:

$\xrightarrow[HNO_3]{H_2SO_4}$



2-Nitroanisole

+



4-nitroanisole