Alcohol Phenol & Ether

Class XII
Board Exam

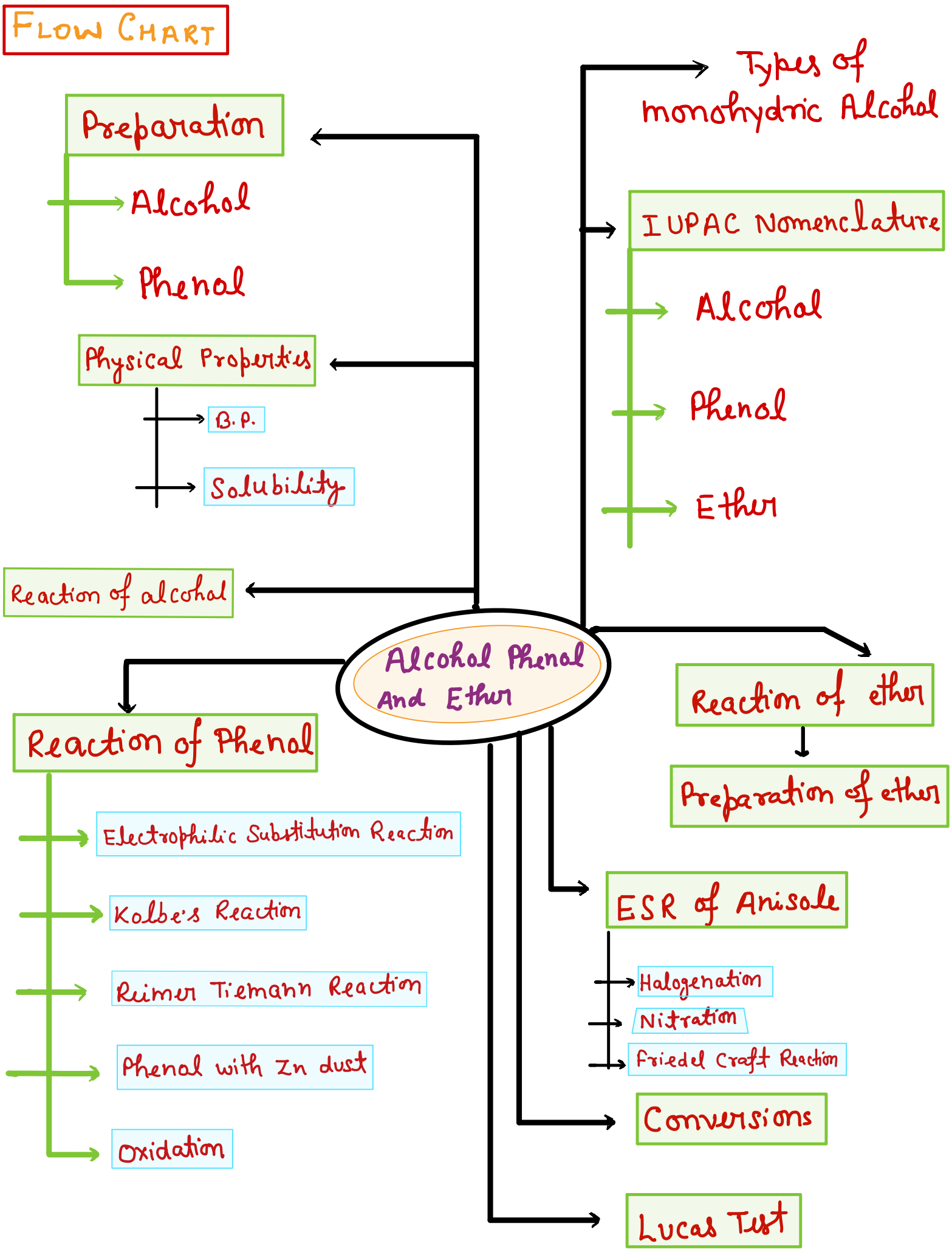
↳ These notes have been verified by top faculties & CBSE Science Toppers

↳ As per updated syllabus

↳ Target 100
↳ Previous Year Q's

Jao Ab Phodo !

Aman Dhattarwal


Flow Chart
Alcohol Phenol And Ether
Preparation
Alcohol
Phenol
Physical Properties
B.P.
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Reaction of alcohal
Reaction of Phenol
Electrophilic Substitution Reaction
Kolbe's Reaction
Reimer Tiemann Reaction
Phenal with Zn dust
Oxidation
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Phenol
Ether
Reaction of ether
Preparation of ether
ESR of Anisole
Halogenation
Nitration
Friedel Craft Reaction
Conversions
Lucas Test

Alcohols, Phenols and Ethers

$R-OH$ | $Ph-OH$ | $R-O-R$

Apni Kaksha

Monohydric Alcohols

Compounds containing $C_{sp^3}-OH$ bond

- Primary Alcohol: $R-CH_2-OH$
- Secondary Alcohol: R_2CH-OH
- Tertiary Alcohol: R_3C-OH

Allylic Alcohols :-

$CH_2=CH-CH_2-OH$

↳ Allylic carbon

[Carbon next to double bond]

Benzylic Alcohols :-

Benzylic Carbon → $C_6H_5-CH_2-OH$

[Carbon next to benzene]

IUPAC Nomenclature of Alcohols

→ The longest carbon chain is numbered starting at the end nearest to the hydroxyl group (-OH).

Alkane − e + ol = Alkanol

Examples :- CH_3-OH : Methanol (Methyl alcohol) ; $CH_3-CH(OH)-CH_3$

↳ IUPAC ↳ Common Name

Propan − 2−ol

(Isopropyl alcohol)

$(CH_3)_3C-OH$: 2− Methylpropan−2−ol

(tert − Butyl alcohol) : [Delhi 2012] 1M

→ $C_6H_5-CH_2-CH_2-OH$: 2− Phenyl ethan−1−ol [CBSE 2016] 1M

→ $CH_2(OH)-CH=C(CH_3)_2$: 3−Methylbut−2−en−1−ol [2015] 1M

→ $CH_3-C(CH_3)(CH_2CH_3)-CH(OH)-CH_3$: 3,3−Dimethylpentan−2−ol

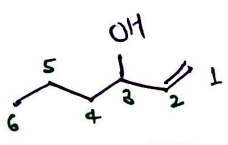
[2018] 1M

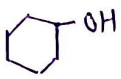
→ $CH_2(OH)-CH(OH)-CH_2(OH)$: Propan−1,2,3−triol

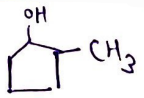
(Glycerol) 1M

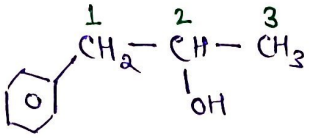
→ Hex−1−en−3−ol

Delhi 2012] 1M Structure →

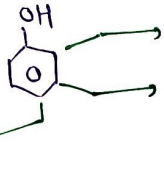


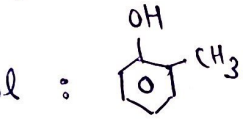
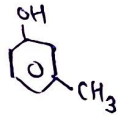
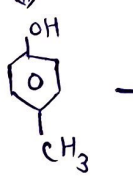
→ Cyclohexanol : 

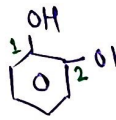
→ 2-Methyl Cyclopentanol : 

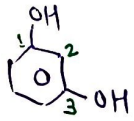
→ 1-Phenylpropan-2-ol :  (CBSE 2010) 1M

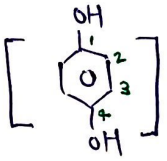
IUPAC Nomenclature of Phenols

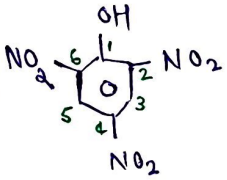
→ Phenal : 
Ortho Position
Meta Position
Para position

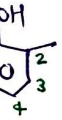
→ Cresol
- 2-Methylphenal : 
- m-Cresol :  → 3-Methyl phenal
- p-Cresol :  → 4-Methyl phenal.

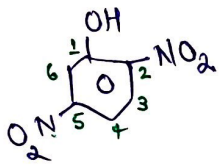
→ Catechol :  : Benzene-1,2-diol

→ Resorcinal :  : Benzene-1,3-dial

→ Quinal (Hydroquinone) : Benzene-1,4-diol 

→ Picric Acid :  : 2,4,6-Trinitrophenal.

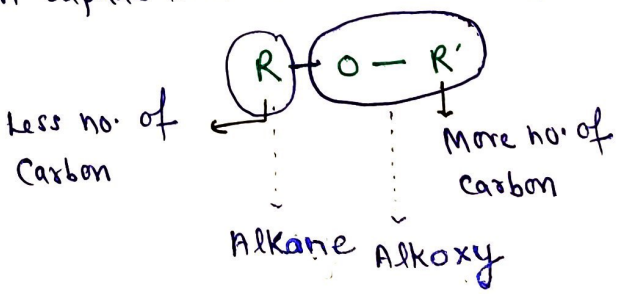
→ 
2,6-Dimethylphenol [2011] 1M

→  : 2,5-Dinitrophenol [Delhi 2015] 1M

IUPAC Nomenclature of Ethers → Alkoxy Alkane

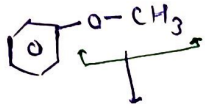
R–O–R'

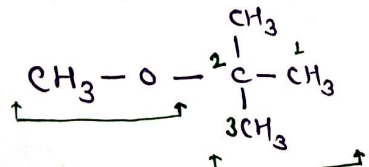
→ Common name of ethers are derived from the names of alkyl / aryl groups written as seperate words in alphabatical order and adding the word "ether" at the end.

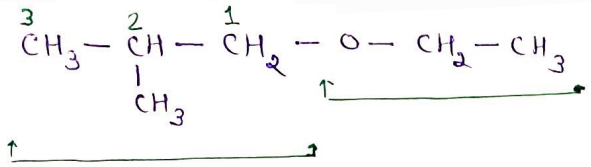


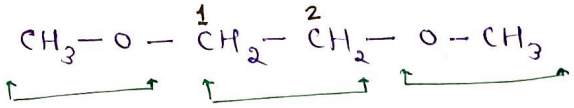
→ CH_3-O-CH_3 [Dimethyl ether]
Methoxy methane

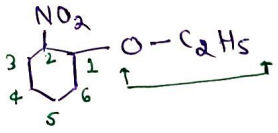
→ $CH_3-O-CH_2-CH_2-CH_3$ [Methyl n-propyl ether]
Methoxy propane

→  Methylphenyl ether
(Anisole) Methoxy benzene

→  2-Methoxy-2-methylpropane
[CBSE 2017] 1M

→  : 1 - Ethoxy - 2 - methyl propane [CBSE 2015] 1M

→  : 1, 2 - Dimethoxy ethane

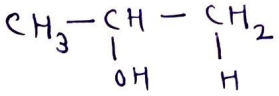
→  : 1 - Ethoxy - 2 - nitrocyclohexane [CBSE 2012C] 1M

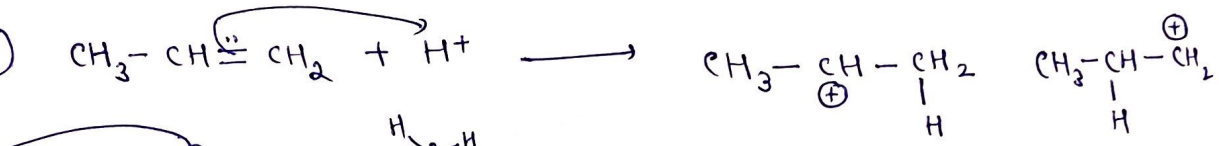
Preparation of alcohols

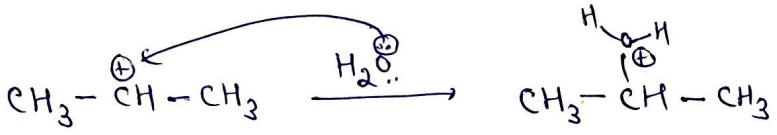
1M

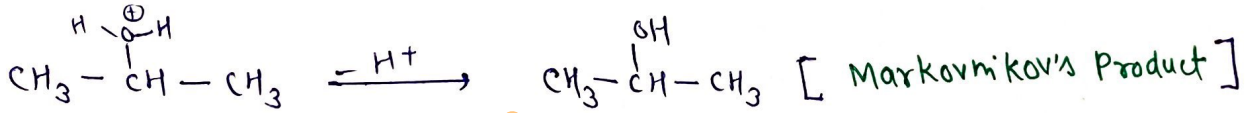
1.] From alkenes :-

[a.] Acid catalysed hydration :- [Delhi 2013]

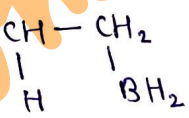
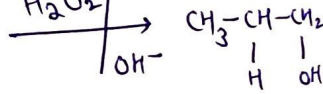
Reaction :- $CH_3-CH=CH_2 + H_2O \xrightarrow{H^+}$  Propan-2-ol

Mechanism -: (i) 

(ii)  (More stable)

(iii)  [Markovnikov's Product]

[b.] Hydroboration - Oxidation Method -:

Reaction : $CH_3-CH=CH_2 \xrightarrow[(BH_3)_2]{B_2H_6}$  $\xrightarrow[OH^-]{H_2O_2}$ 

[Anti markovnikovs Product]

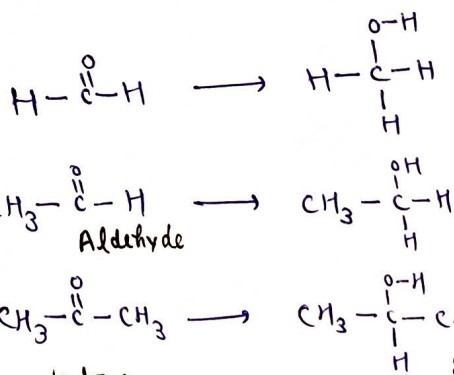
[Delhi 2013] 1M [CBSE 2016]

2.] From Carbonyl compounds -:

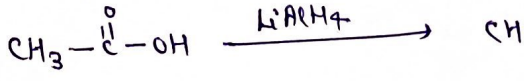
(a.) → Reduction of aldehyde and ketone :-

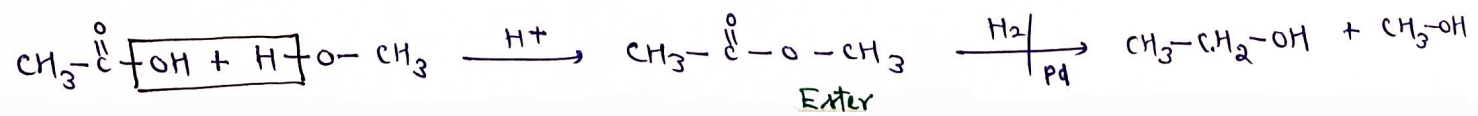
Reducing agent : $NaBH_4$ | $LiAlH_4$ | H_2 with Pd

Only for Ketone/Aldehyde → Ketone/Aldehyde/Acid Ester



(b.) → Reduction of Carboxylic Acid -:

→ 

→ 

3.] From Grignard Reagents –:

Reaction : $R-\overset{\delta-}{C}=O^{\delta-}$ ... $R'\overset{\delta-}{\leftarrow}Mg^{\delta+}-X \longrightarrow R-C(-O^{\ominus}Mg^{\oplus}X)-R' \xrightarrow{H_2O} R-C(-OH)-R' + Mg(OH)X$

(a) $H-CHO + CH_3MgBr \longrightarrow H-CH(OMgBr)-CH_3 \xrightarrow{H_2O} H-CH(OH)-CH_3$

Formaldehyde — Methyl magnesium bromide. — 1°- Alcohol

(b) $CH_3-CHO + CH_3MgBr \longrightarrow CH_3-CH(OMgBr)-CH_3 \xrightarrow{H_2O} CH_3-CH(OH)-CH_3$ 2°- Alcohol

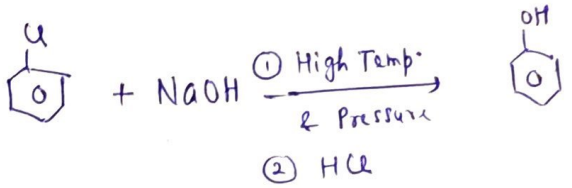
(c) $CH_3-CO-CH_3 + CH_3MgBr \longrightarrow CH_3-C(OMgBr)(CH_3)-CH_3 \xrightarrow{H_2O} CH_3-C(OH)(CH_3)-CH_3$ 3° Alcohol

[Delhi 2010]

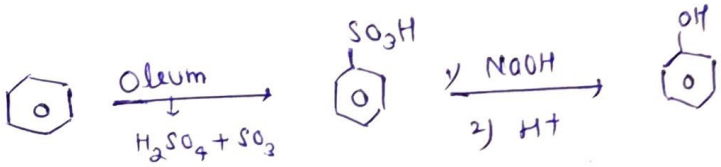
1M

Preparation of Phenal

1. From Haloarenes –:

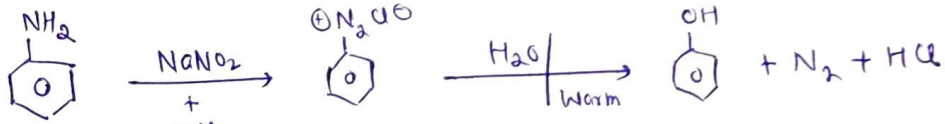


2. From Benzenesulphonic Acid –:

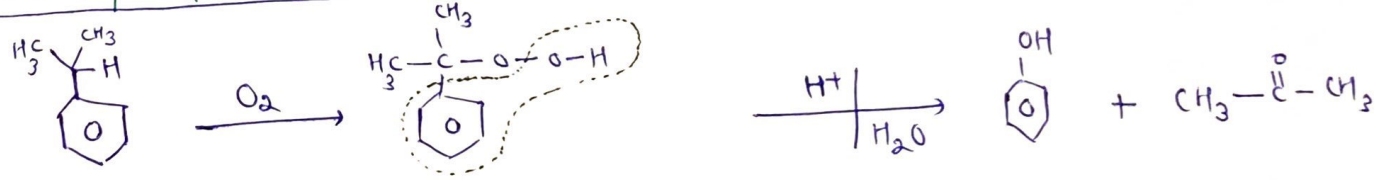


3. From diazonium salt –:

Aniline



4. Cumene Hydroperoxide Method –:



Cumene — Cumene Hydroperoxide

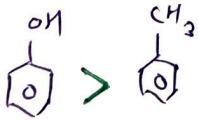
Physical Properties

Boiling Point –: B.P. of alcohols and phenols ↑ as no. of carbon atoms increases

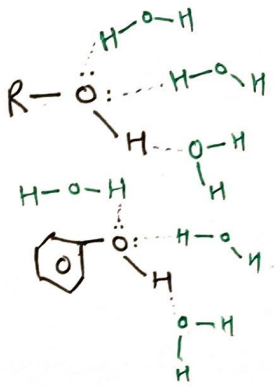
→ In alcohols –: As branching ↑es ⇒ B.P. ↓es : This is because of decrease in Vander Waals forces with decrease in surface area.

→ B.P. : $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{C}-OH$ < $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-OH$ < $CH_3-CH_2-CH_2-CH_2-OH$

→ B.p. of alcohols and phenols (higher in comparison to hydrocarbons, ethers haloalkanes and haloarenes of comparable molecular masses. This is because of hydrogen bonding in alcohols and phenols. [CBSE 2012] 1M

→  : B.P. similarly B.P. order : 

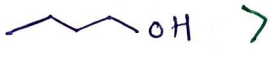
→ CH_3-CH_2-OH > CH_3-O-CH_3 : B.P.



Solubility -: Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water.

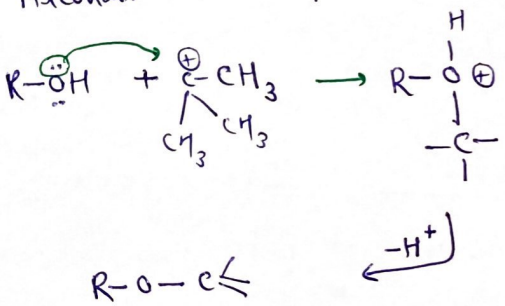
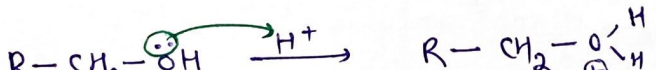
→ Solubility ↓es ⇒ size of alkyl / aryl group ↑es

(Hydrophobic part.)

→ Solubility order :  > 

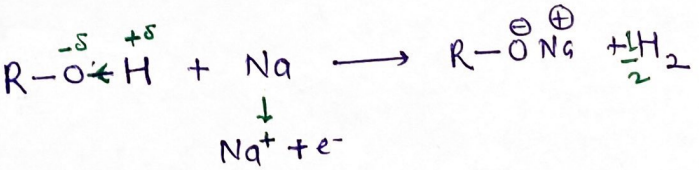
Chemical Reactions

→ R — O — H

- Breaking of oxygen and hydrogen bond.
  - Alcohols as nucleophile :-
  - 
- Breaking of carbon and oxygen bond
  - → Protonated alcohols as electrophiles
  - 
  - 

Apni Kaksha :)

Acidity of alcohols & phenols -:

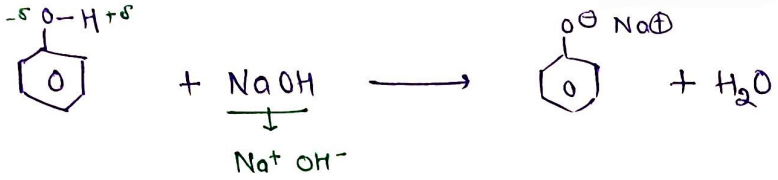


→ 

Phenol + Na → $Na^+ + e^-$

Sodium Phenoxide + $\frac{1}{2}H_2$

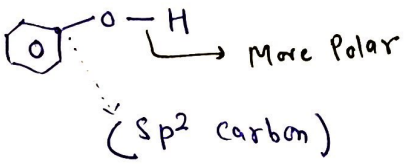
This reaction shows that alcohols and phenols can donate H^+, means that they are acidic.

→ 

#] The acidic character of alcohols is due to the polar nature of –O–H bond. An electron releasing group (–CH_3 / –C_2H_5 etc.) increases ele n density on oxygen trendi to derease the polarity of –O–H bond. This derease the acidic strength.

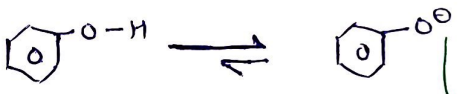
$$R \rightarrow CH_2 \rightarrow O-H \; > \; \begin{matrix} R \\ R \end{matrix}\!\!>\!CH \rightarrow O-H \; \gg \; \begin{matrix} R \\ R \\ R \end{matrix}\!\!>\!C \rightarrow O-H$$

#] Phenols are more acidic than alcohols ? [CBSE 2015] (1M)

→ R–O–H and 

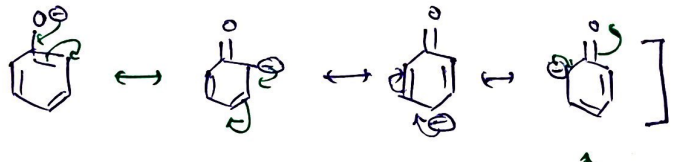
R–O–H → Less Polar

→ Ionisation of alcohol : $R-O-H \rightleftharpoons R-O^{\ominus} + H^+$ (This ⊖ charge is localised on oxygen atom.)

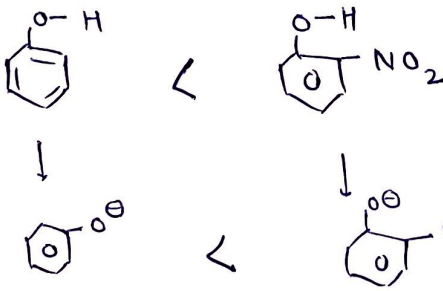
Ionisation of phenol : 

This ⊖ve charge is delocalised due to conjugation

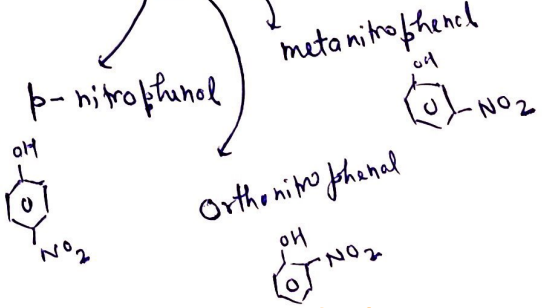
Due to resonance phenoxide is stable than alkoxide.

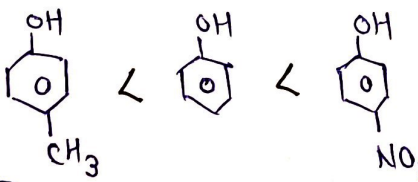

Resonating structure of phenoxide Ion.

NOTE –: In resonating structure of phenoxide ion ⊖ve charge is present at ortho and para position. So, ⊖ve charge stabilising groups (–I / –M) can increase stability of substituted phenoxide ion. Thus it can increase the acidity.

→ 

→ POM Phenol : Ka



→ 

[CBSE 2017] (1M)

→ **Esterification :–** (Formation of ester) # Alcohols | Phenols + carboxylic acid or its derivatives

→ 

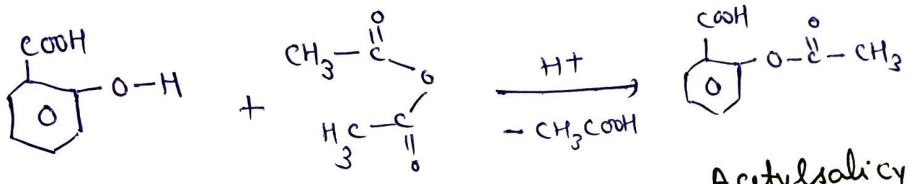
This oxygen comes from alcohol / phenol.

Because reaction is reversible, so remove the water as soon as it formed.

→ $CH_3-CH_2-O-H + H-O-C(=O)-CH_3 \overset{H^+}{\rightleftharpoons} CH_3-CH_2-O-C(=O)-CH_3$

→ $R-O-H + Cl-C(=O)-R' \xrightarrow[\text{Base}]{\text{Pyridine}} R-O-C(=O)-R' + HCl$

Pyridine is used to neutralise HCl and to make reaction progressive in forward direction.

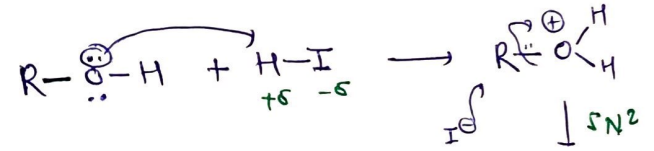
→ 

Salicylic Acid

Acetylsalicylic acid [Aspirin]

➡ **Reactions involving cleavage of Carbon – Carbon bond in alcohols :–**

1. **Reaction with HX [HCl | HBr | HI] :–**



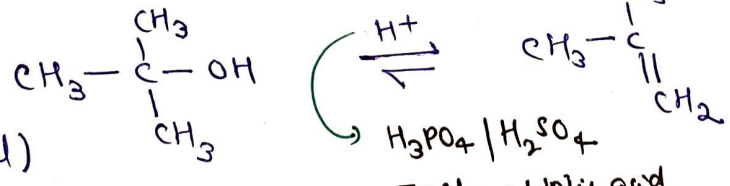
$R-I + H_2O$

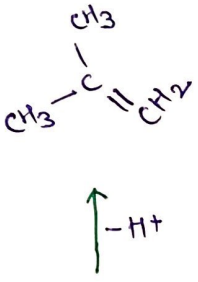
2. **Reaction with $SOCl_2$ | PCl_3 | PCl_5 :–**

$CH_3-CH_2-OH \xrightarrow[PCl_3 \text{ or } PCl_5]{SOCl_2 \text{ or}} CH_3-CH_2-Cl$ [CBSE 2015C] (1M)

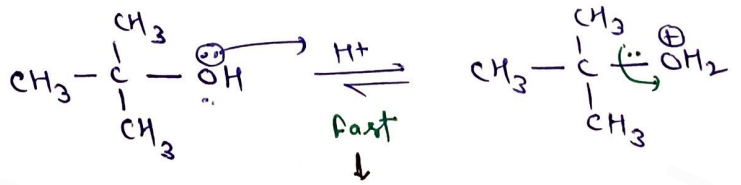
3. **Dehydration :–** [Removal of H_2O from a molecule]

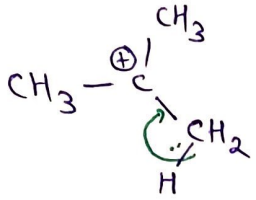
Reaction :





Mechanism :–





→ $CH_3-CH_2-OH \xrightarrow[\Delta]{H^+} CH_2=CH_2$

[CBSE 2019 | 2013 Delhi 2015C]

$CH_3-CH_2-OH \xrightarrow{H^+} CH_3-CH_2-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} CH_2-\overset{\oplus}{C}H_2 \xrightarrow{-H^+} CH_2=CH_2$

→ $CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{85\%\ H_3PO_4} CH_3-CH=CH_2$

4.) Oxidation :-

$R-\underset{R'}{C}(H)(-O-H) \longrightarrow R-\underset{R'}{C}(=O)$: Removal of di-hydrogen ⇓ Dehydrogenation

Alcohal → Ketone / Aldehyde

PCC / CrO_3 ← Weak oxidising agent

1° Alcohol → Aldehyde → Acid

Strong oxidising agent → $KMnO_4/H^+$

→ $CH_3-CH_2-OH \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-H$

PCC : Pyridinium Chlorochromate → $(C_5H_5N \cdot CrO_3 \cdot HCl)$

$\xrightarrow[H^+]{KMnO_4}$ → $CH_3-\overset{O}{\overset{\|}{C}}-OH$

Sec- Alcohal : $CH_3-\underset{OH}{CH}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$: Ketone.

ter. Alcohal : $CH_3-\underset{CH_3}{\overset{CH_3}{C}}(-OH)-CH_3 \xrightarrow{CrO_3} \times$ Because there is no C-H bond.

→ Cu / 300°C

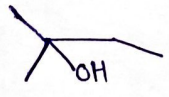
Delhi 2015

oxidation ←

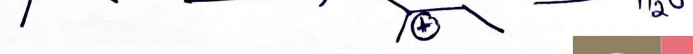
a.) $CH_3-CH_2-OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-H$

b.) $CH_3-\underset{OH}{CH}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Dehydration : c.) $CH_3-\underset{CH_3}{\overset{CH_2-H}{C}}-OH \xrightarrow{(-H_2O)} CH_3-\underset{CH_3}{\overset{CH_2}{C}}$

Question:- Alkene → 

[CBSE 2019] 1M



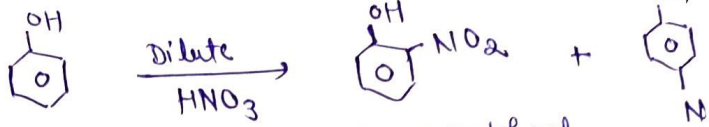
H_3O^+ → H_2O

Reactions of Phenol

① Electrophilic aromatic substitution —: Phenol and phenoxide ion, direct the incoming electrophile to ortho and para positions in the ring as these position becomes electron rich due to resonance effect caused by $-OH$ & $-O^{\ominus}$ group.

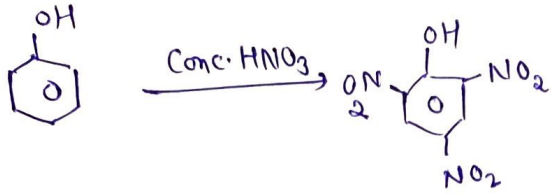
→ Nitration :—

(a)



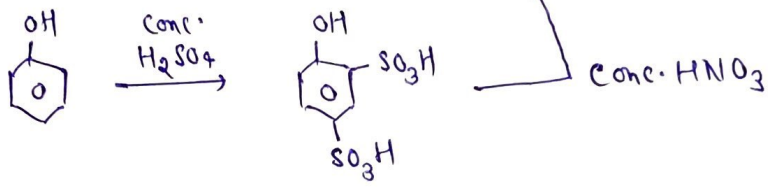
Ortho-Nitrophenol Para-Nitrophenol

→



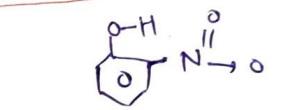
Picric acid [2, 4, 6-Trinitrophenol]

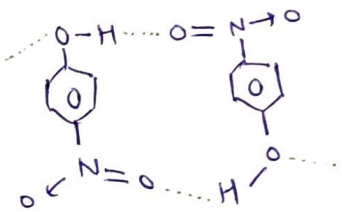
→



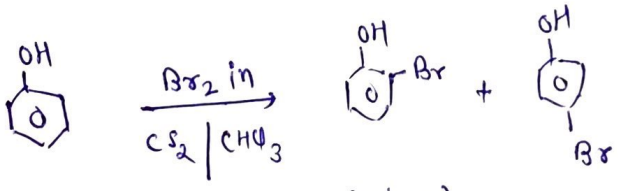
Question :— o-Nitrophenol is more steam volatile than p-Nitrophenol, Why? [Delhi 2019 | CBSE 2014]

Answer —: o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

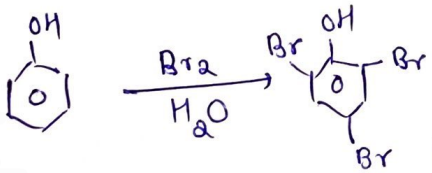




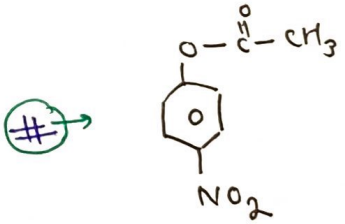
(b) Halogeration :—

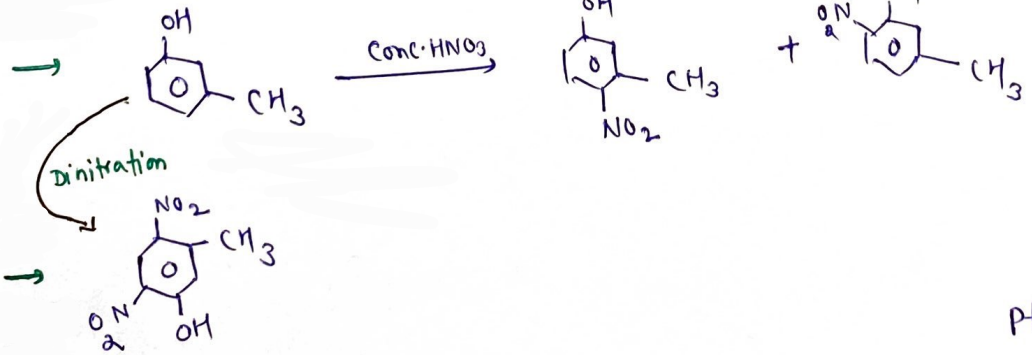


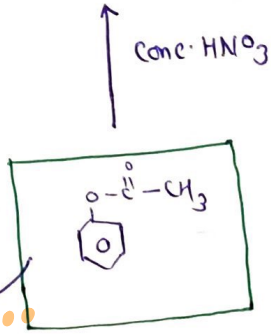
(Minor) (Major)



White ppt of [2, 4, 6-Tribromophenol]

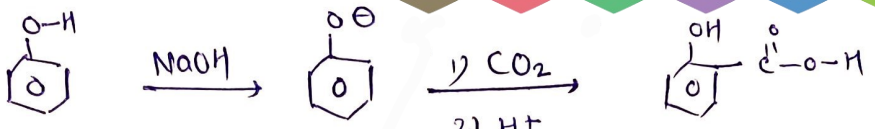






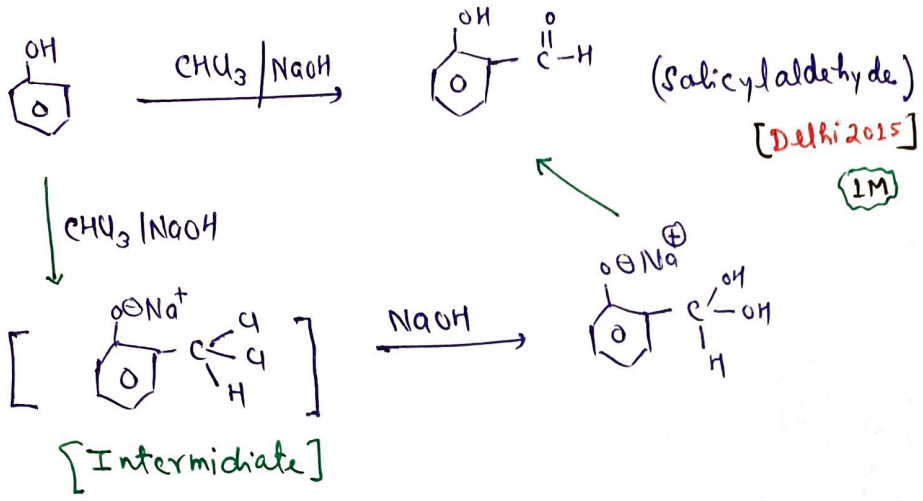
2.) **Kolbe's Reaction** :-

[Delhi 2014C] (1M)



2-Hydroxy benzoic acid
(Salicylic acid)

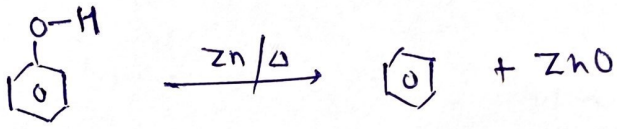
3. **Reimer-Tiemann Reaction** :-



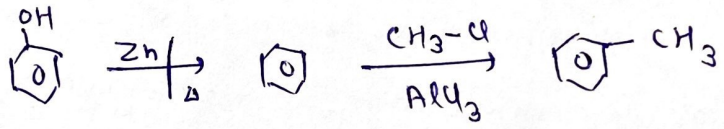
On treating phenol with chloroform and NaOH, a $-\overset{O}{\overset{\|}{C}}-H$ group is introduced at ortho position of benzene ring. This reaction is known as RT Reaction.

(1M) [2011 | 2012 | 2019] CBSE

4. **Phenol with Zn dust** :-

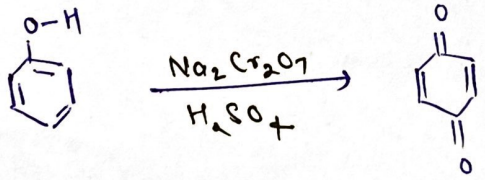


→ Phenol to toluene :



[Delhi 2013C]
(1M)

5. **Oxidation** :-

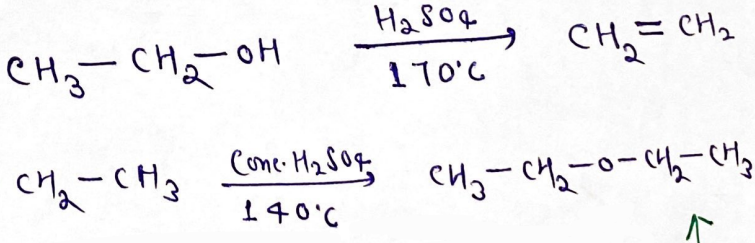


Benzoquinone

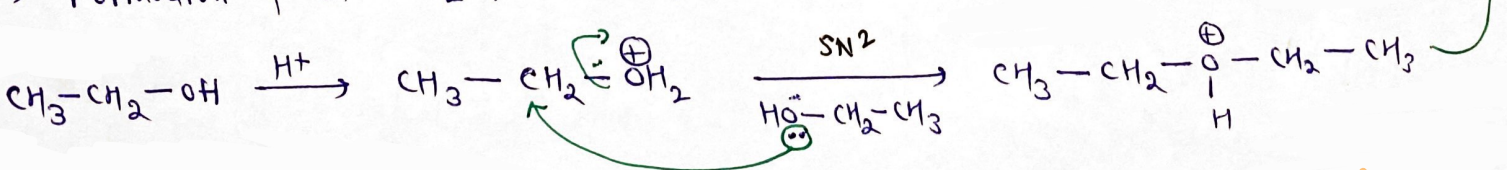
Ethers

Prepration of ethers :-

1) **By dehydration of alcohols** :-



→ Formation of ether [Mechanism]



Apni Kaksha

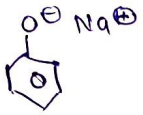
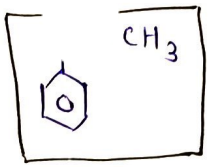
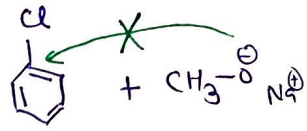
② Williamson Synthesis —:

Alkyl halide + Sodium Alkoxide ⟶ Ether

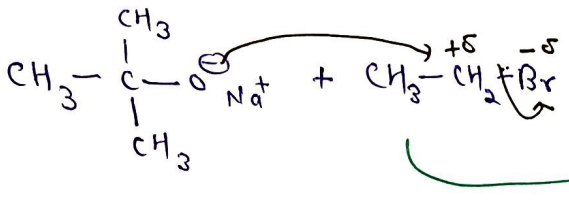
→ $R-X + R'-O^{\ominus}Na^{\oplus} \longrightarrow R-O-R' + NaX$

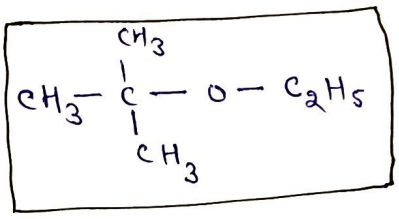
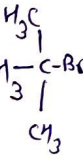
(1M) [Delhi 2010, CBSE 2010]

($R-X$: Methyl | 1°/2°) ($R'-O^{\ominus}Na^{\oplus}$: Phenyl | 1°/2°/3°/Methyl)

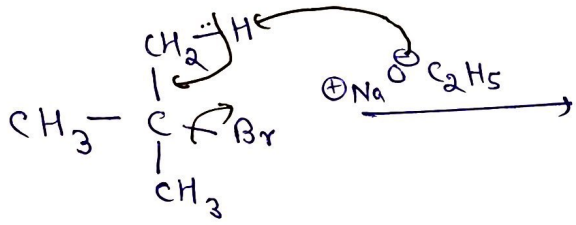
⇒  + CH_3-Br ⟶  ⟵ 

→ $CH_3-CH_2-O^{\ominus}Na^{\oplus} + CH_3-\overset{\delta+}{CH_2}\cdots\overset{\delta-}{Br} \longrightarrow CH_3-CH_2-O-CH_2-CH_3$

→ 

 ⟵ $C_2H_5-O^{\ominus}Na^{+}$ + 

3° Alkyl Halide

→ 

Alkene

Chemical Reaction of ether

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

Mechanism —: $R-\ddot{O}-R' \xrightarrow[HX]{H^+} R-\overset{\oplus}{O}(H)-R' \xrightarrow{X^{\ominus}}$

If R' is a small alkyl group then ⇓ S_N2 → $R'-X$ + $R-OH$

If R or R' is 3° alkyl halide ⇓ S_N1 → R^+ + $R'-OH$

[If R is 3° alkyl group] $R^+ \xrightarrow{X^{\ominus}} R-X$

→ $CH_3-O-CH_3 \xrightarrow[H^+]{HI} CH_3-\overset{\oplus}{O}(H)-CH_3 \xrightarrow{I^{\ominus}} CH_3-I + CH_3-OH$

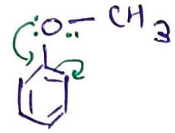
→ $CH_3-O-CH_2-CH_3$ $\xrightarrow{HI}$ $CH_3-\overset{\oplus}{O}(H)-CH_2-CH_3$ $\xrightarrow{S_N2}$ CH_3-I + CH_3-CH_2-OH

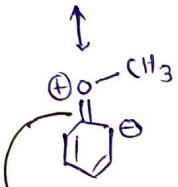
(I⊖ attacks)

→ $H_3C-C(CH_3)_2-O-CH_3$ $\xrightarrow{HI}$ $\xrightarrow{H^+}$ $CH_3-C(CH_3)_2-\overset{\oplus}{O}(H)-CH_3$ → $H_3C-C^{\oplus}(CH_3)_2$ + CH_3-OH

[CBSE 2015] 1M

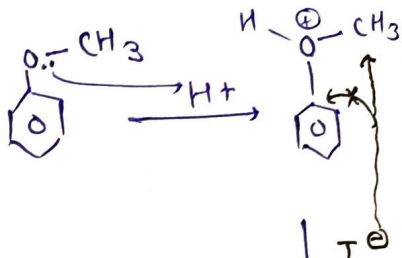
I⊖ ← +I

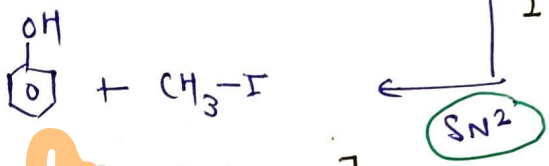
→  $\xrightarrow{HI}$  + CH_3-I



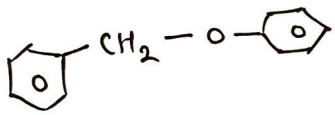
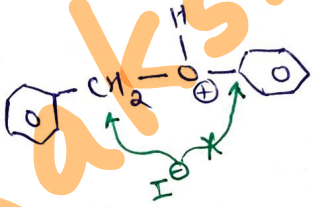
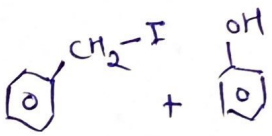
Due to Double bond character it is tough to break this bond.

Mechanism-:

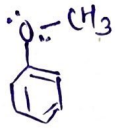




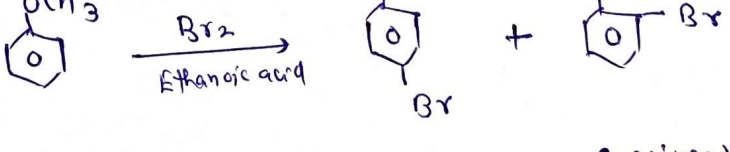
[Delhi 2010C]

→  $\xrightarrow{HI}$  → 

Electrophilic Substitution Reaction of Anisol

→ **Anisol** :  (−O−CH_3 is a +M group which is ortho − para directing in nature)

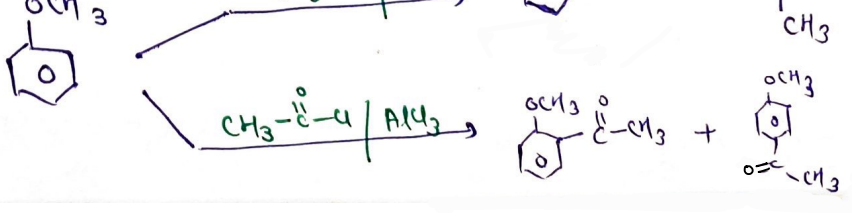
q.> **Halogenation** :



[Delhi 2015C] 1M

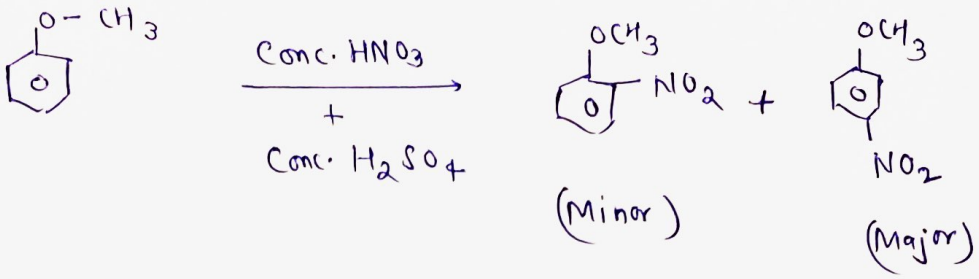
(Major) (Minor)

b.> **Friedel Crafts reaction** −:



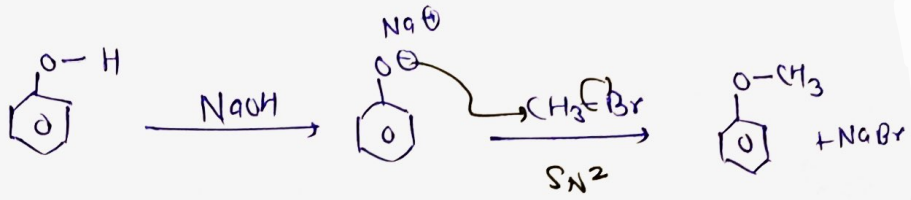
[Delhi 2011 | 2010] 1M

c.) **Nitration :—**

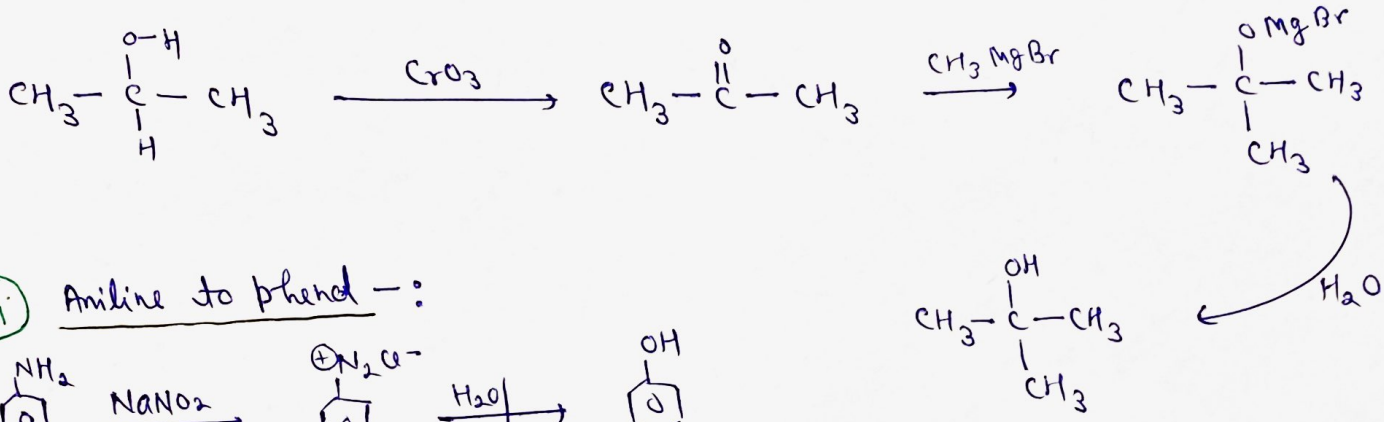


Conversions

(i) **Phenol to anisole :—**



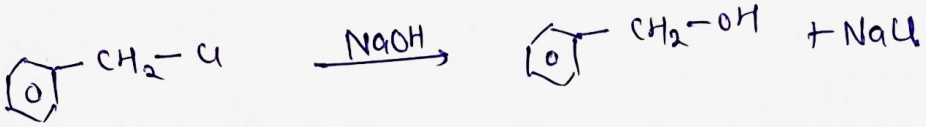
(ii) **Propan-2-ol to 2-methyl propan-2-ol :—**



(iii) **Aniline to phenol —:**

Above three ← [Delhi 2015]
(3M)

(iv) Benzyl chloride ⟶ Benzyl Alcohol



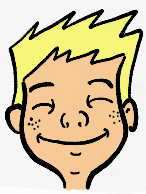
Lucas Test → To differ. 1°/2°/3° Alcohol
→ Phenol does not give this test.

Lucas Reagent → $ZnCl_2$ / HCl

(1) $R-CH_2-OH \xrightarrow[HCl]{ZnCl_2} R-CH_2-Cl$ → Turbidity aft. 30 min.

(2) $R-\underset{R}{\underset{|}{CH}}-OH \xrightarrow[HCl]{ZnCl_2} R-\underset{R}{\underset{|}{CH}}-Cl$: Turbidity within 5 min.

(3) $R-\overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow[HCl]{ZnCl_2} R-\overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}}-Cl$: Turbidity with second.



समाप्त