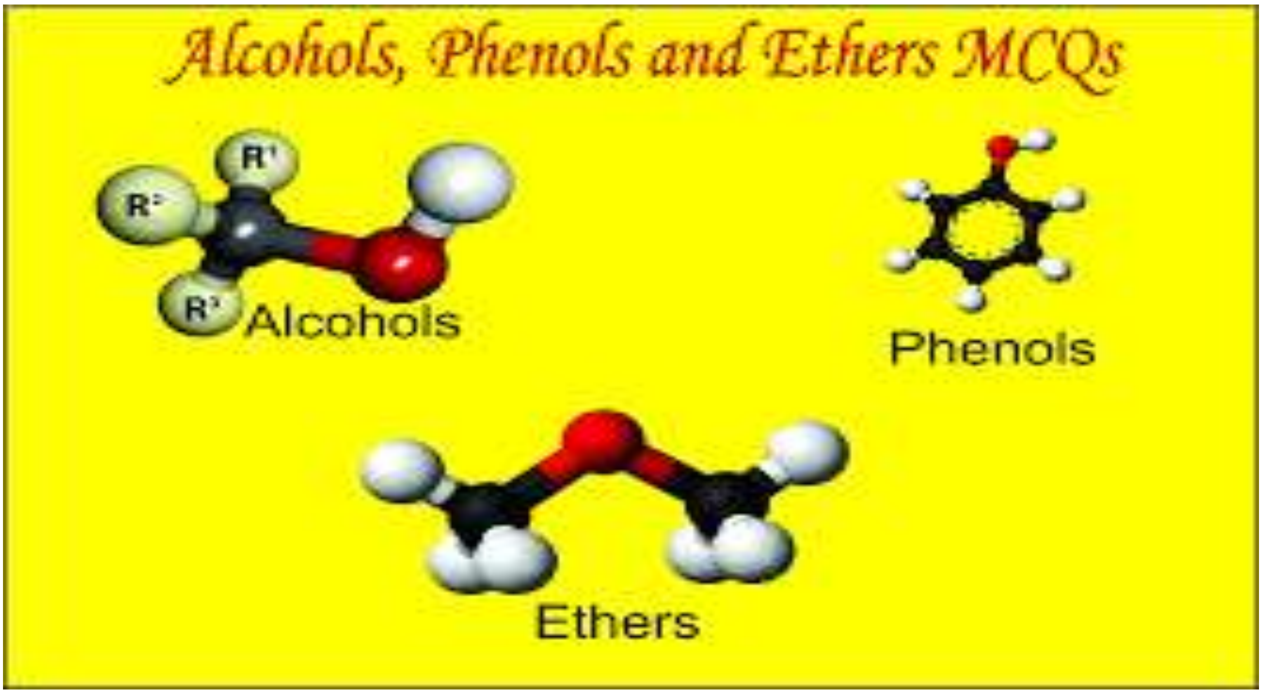


Compound	Common name	IUPACname
$CH_3 - OH$	Methyl alcohol	Methanol
CH_3-CH_2-CH_2-OH	n-Propyl alcohol	Propan-1-ol
CH_3-CH-CH_3 (OH on CH)	Isopropyl alcohol	Propan-2-ol
CH_3-CH-CH_2-CH_3 (OH on CH)	sec-Butyl alcohol	Butan-2-ol
CH_3-CH-CH_2-OH (CH_3 on CH)	Isobutyl alcohol	2-Methyl propan-1-ol
CH_3-C-OH (CH_3 above and below C)	tert-Butyl alcohol	2-Methyl propan-2-ol

ALCOHOLS, ETHERS AND PHENOLS

1. INTRODUCTION

The compounds in which hydroxyl group (–OH) is attached to a saturated carbon atom are called as **Alcohols**. The compounds in which a hydroxyl group is attached to an unsaturated carbon atom of a double bond are called as **Enols**. The saturated carbon may be that of an alkyl, alkenyl, alkynyl, cycloalkyl or benzyl group. However, if a hydroxyl group is attached to a benzene ring, the compounds are called as **Phenols**.

The alcohols are further classified as : **Monohydric** (containing one –OH group), **Dihydric** (containing two –OH groups) and **Trihydric** (containing three –OH groups).

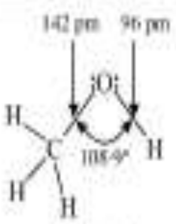
Alcohols find usage in industry as well as day to day life. For example, ordinary spirit used for polishing wooden furniture is chiefly ethanol. Sugar, cotton, paper are all made up of compounds containing –OH groups. Phenols are used in several important polymers such as *Bakelite* and in several drugs such as *Aspirin*. Ethers are commonly used as solvents and anaesthetics.

2. CLASSIFICATION

$CH_3—OH$	Methanol	
$R—CH_2—OH$	1° Alcohol	Primary
$R—CH(R)—OH$	2° Alcohol	Secondary
$R—C(R)(R)—OH$	3° Alcohol	Tertiary
R—O—R	Symmetrical Ether	
R—O—R'	Unsymmetrical Ether	

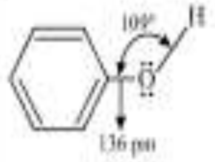
3. STRUCTURES OF FUNCTIONAL GROUPS

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. The following figure depicts structural aspects of methanol, phenol and methoxymethane.



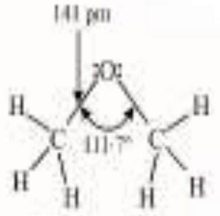
Methanol

Bond angle is slightly less due to LP-LP repulsion.



Phenol

Lone pair of oxygen is delocalised on ring due to which C—O bond length is less.



Methoxymethane

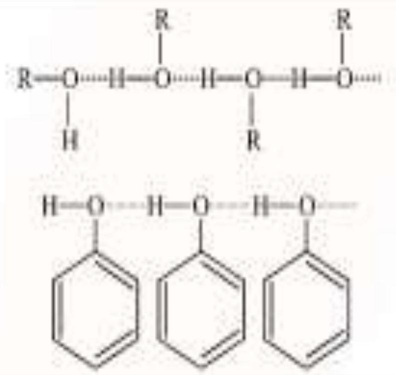
Bond angle in methoxymethane is more than tetrahedral angle due to repulsive interaction between the two bulky (R) groups. The C—O bond length is same as in alcohols.

4. PHYSICAL PROPERTIES

4.1 Boiling Point

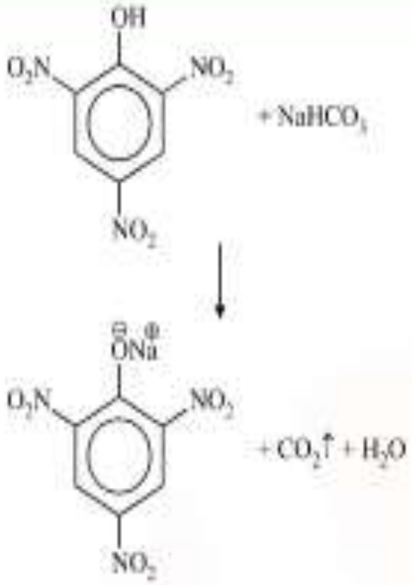
The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling point decreases with increase in branching (decrease in Van der Waals forces due to decrease in surface area).

The –OH group in alcohols and phenols contains a hydrogen, bonded to an electronegative oxygen atom. Therefore, it is capable of forming intermolecular hydrogen bond, strength of which is even greater than amine.



It is due to the presence of strong intermolecular hydrogen bonding that alcohols and phenols have higher boiling points corresponding to other classes of compounds, namely, hydrocarbons, ethers and haloalkanes/haloarenes, amines of comparable molecular masses.

Their boiling points are lower than carboxylic acid which have even more strong H-bond. For isomeric alcohols boiling points decreases with increase in branching due to decrease in van der Waals forces with decrease in size. **The order of boiling point is 1° alcohol > 2° alcohol > 3° alcohol.**



15.5.4 $FeCl_3$ Test

Phenol gives characteristic purple colour with $FeCl_3$ but alcohols do not react with $FeCl_3$. Carboxylic acids also form buff coloured precipitate with $FeCl_3$. Only acetic acid forms red coloured precipitate with $FeCl_3$, so it can be used as a test for acetate salts.

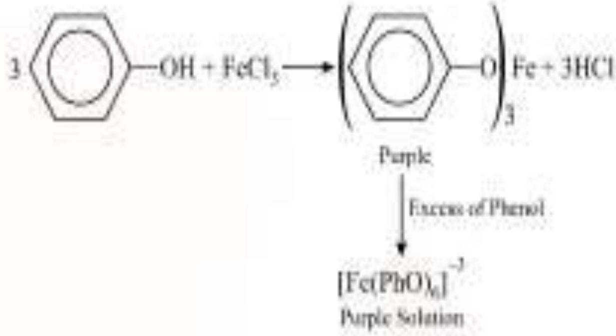


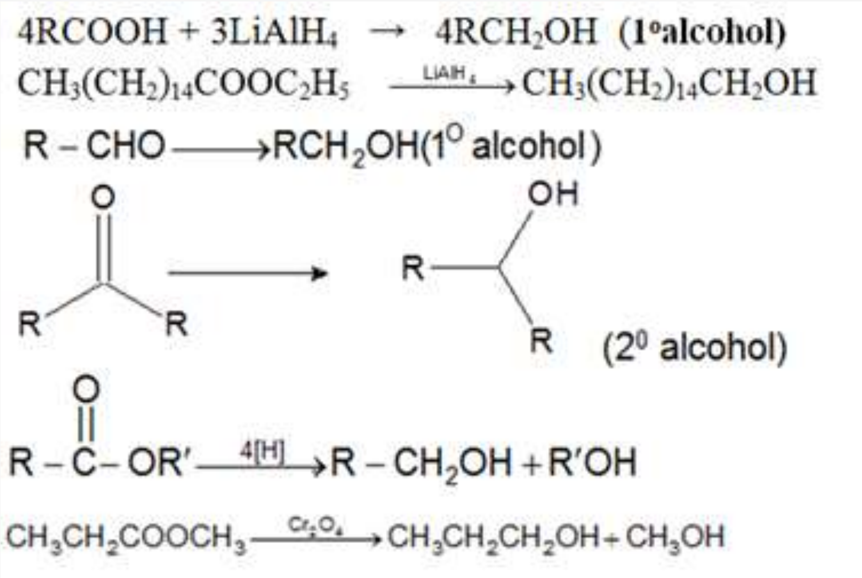
Table 1 : Physical Properties of Selected Alcohols

IUPAC Name	Common Name	Formula	MP(°C)	BP(°C)	Density
methanol	methyl alcohol	CH_3OH	– 97	65	0.79
ethanol	ethyl alcohol	CH_3CH_2OH	– 114	78	0.79
1-propanol	n-propyl alcohol	$CH_3CH_2CH_2OH$	– 126	97	0.80
2-propanol	isopropyl alcohol	$(CH_3)_2CHOH$	– 89	82	0.79
1-butanol	n-butyl alcohol	$CH_3(CH_2)_3OH$	– 90	118	0.81
2-butanol	sec-butyl alcohol	$CH_3CH(OH)CH_2CH_3$	– 114	100	0.81
2-methyl-1-propanol	isobutyl alcohol	$(CH_3)_2CHCH_2OH$	– 108	108	0.80
2-methyl-2-propanol	t-butyl alcohol	$(CH_3)_3COH$	25	83	0.79
1-pentanol	n-pentyl alcohol	$CH_3(CH_2)_4OH$	– 79	138	0.82
3-methyl-1-butanol	isopentyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	– 117	132	0.81
2, 2-dimethyl -1-propanol	neopentyl alcohol	$(CH_3)_3CCH_2OH$	52	113	0.81
cyclopentanol	cyclopentyl alcohol	cyclo-C_5H_9OH	– 19	141	0.95
1-hexanol	n-hexanol	$CH_3(CH_2)_5OH$	– 52	156	0.82
cyclohexanol	cyclohexyl alcohol	cyclo-$C_6H_{11}OH$	25	162	0.96
1-heptanol	n-heptyl alcohol	$CH_3(CH_2)_6OH$	– 34	176	0.82
1-octanol	n-octyl alcohol	$CH_3(CH_2)_7OH$	– 16	194	0.83
1-nonanol	n-nonyl alcohol	$CH_3(CH_2)_8OH$	– 6	214	0.83
1-decanol	n-decyl alcohol	$CH_3(CH_2)_9OH$	6	233	0.83
2-propen-1-ol	allyl alcohol	$H_2C{=}CH{-}CH_2OH$	– 129	97	0.86
phenylmethanol	benzyl alcohol	$Ph{-}CH_2OH$	– 15	205	1.05
diphenylmethanol	diphenylcarbinol	Ph_2CHOH	69	298	
triphenylmethahnol	triphenylcarbinol	Ph_3COH	162	380	1.20
1, 2-ethanediol	ethylene glycol	$HOCH_2CH_2OH$	– 13	198	1.12
1, 2-propanediol	propylene glycol	$CH_3CH(OH)CH_2OH$	– 59	188	1.04
1, 2, 3-propanetriol	glycerol	$HOCH_2CH(OH)CH_2OH$	18	290	1.26

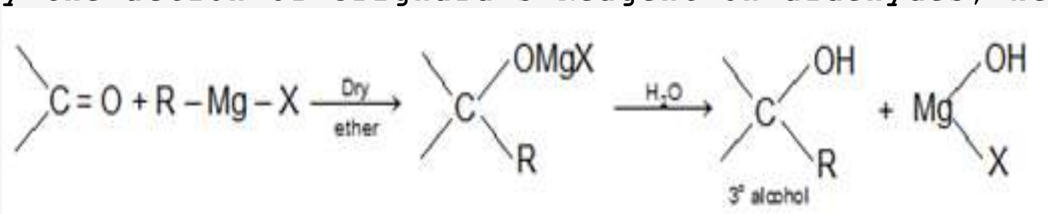
Alcohols

Preparation of Alcohols:

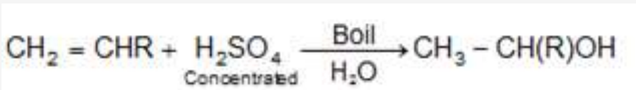
- **By hydrolysis of haloalkanes :** R−X + aq. KOH →ROH +KX
- **By reduction of Carbonyl compounds**



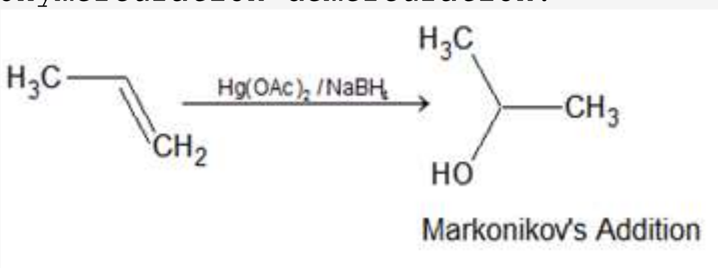
- **By the action of Grignard's Reagent on aldehydes, ketones and esters**



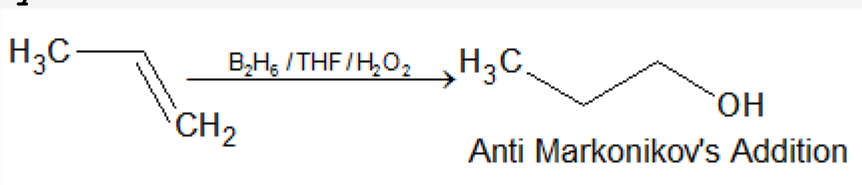
- **By Aliphatic Primary Amines:** $RCH_2NH_2 + HNO_2 \rightarrow RCH_2OH + N_2 + H_2O$
- **Hydration of alkenes:**



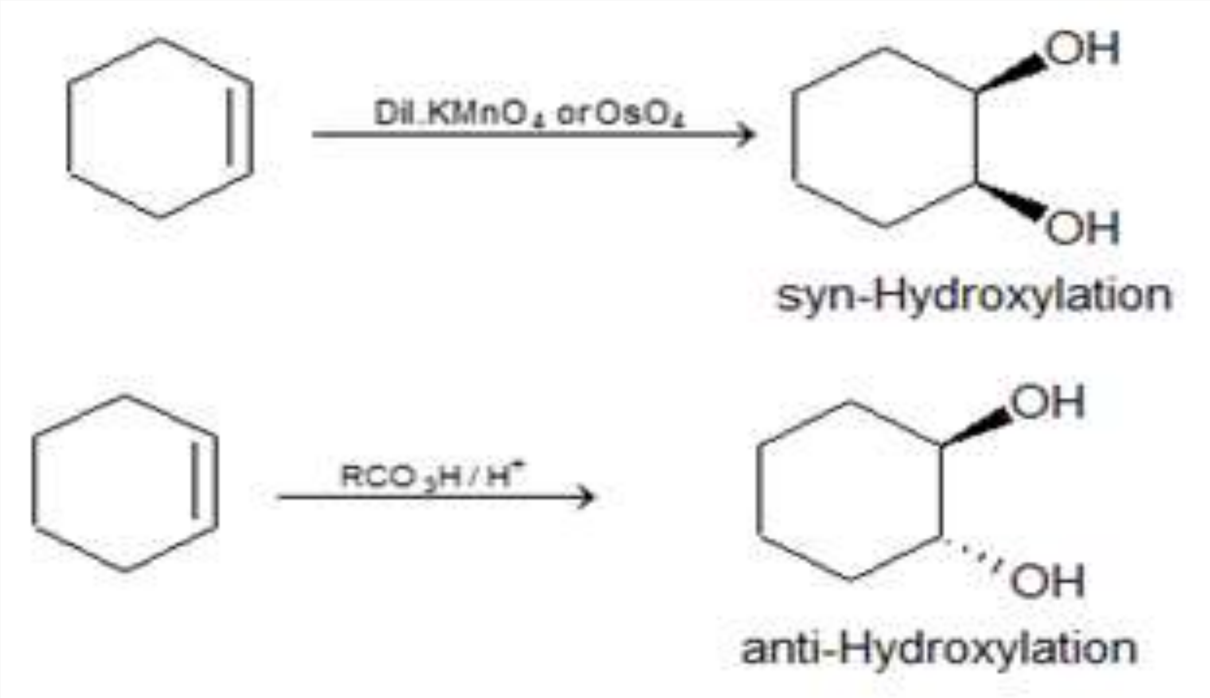
- Oxymercuration-demercuration:



- **Hydroboration-oxidation:**



- **Hydroxylation of alkenes:**



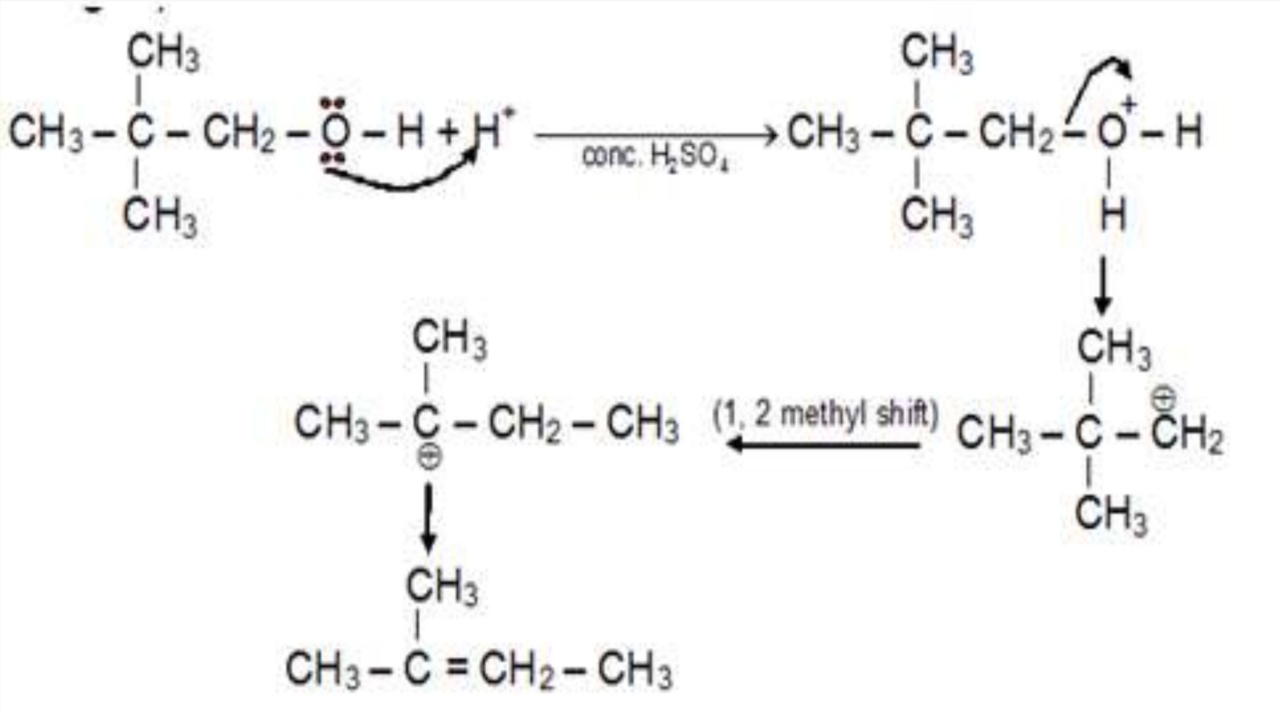
Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

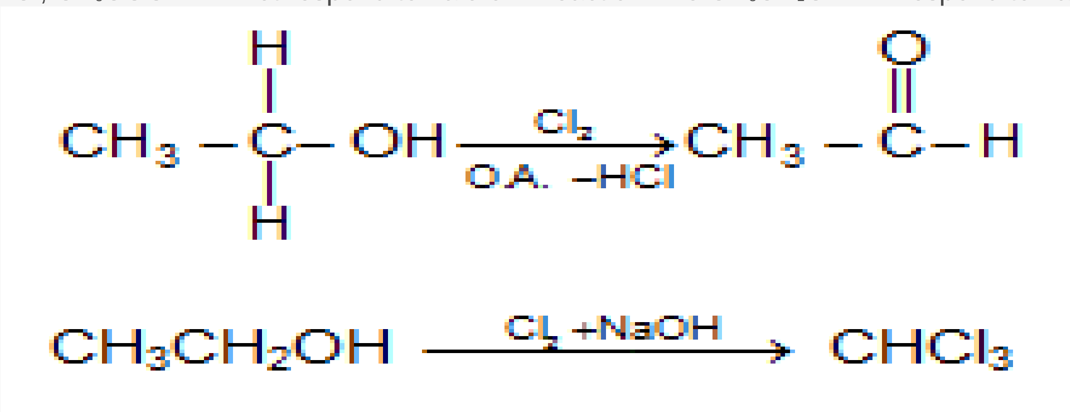
Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:** $ROH + Na \rightarrow 2RO^{+}Na^{-} + H_2$
- **Formation of Halides:**
  - $3ROH + P + I2 \rightarrow 3RI + H_3PO_3$
  - $ROH + SOCl_2/PCl_3/PCl_5 \rightarrow RCl$
  - $ROH + HX \rightarrow RX$
  - $ROH + NaBr, H_2SO_4 \rightarrow R\text{-}Br$
  - $ROH + Zn + HCl \rightarrow R\text{-}Cl$
  - $R_2C\text{-}OH$ alcohol + $HCl \rightarrow R_2CCl$
- **Reaction with HNO_3:** $R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$
- **Reaction with carboxylic acid (Esterification) :** $R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$
- **Reaction with Grignard reagent:** $R'OH + RMgX \rightarrow RH + R'OMgX$
- **Reduction of alcohol :** $ROH + 2HI + \text{Red } P \rightarrow RH + I_2 + H_2O$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: 3° > 2° > 1

- **Satyzeff's Rule :** Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol**:
  $RCH_2\text{-}OH + [O] \rightarrow RCHO \rightarrow RCOOH$
  $RCH_2\text{-}OH + [O] + PCC \rightarrow RCHO$
- **Haloform Reaction:** Compound containing CH_3CO- group (or compound on oxidation gives CH_3CO – group) wh ich is attached with a C or H, in presence of halogen and mild alkali gives haloform.$CH_3\text{-}CH_2\text{-}COCH_2\text{-}CH_3$, CH_3-CO-Cl, CH_3COOH will not respond to haloform reaction wile CH_3CH_2OH will respond to haloform Reaction.



?

Test for Alcohols:

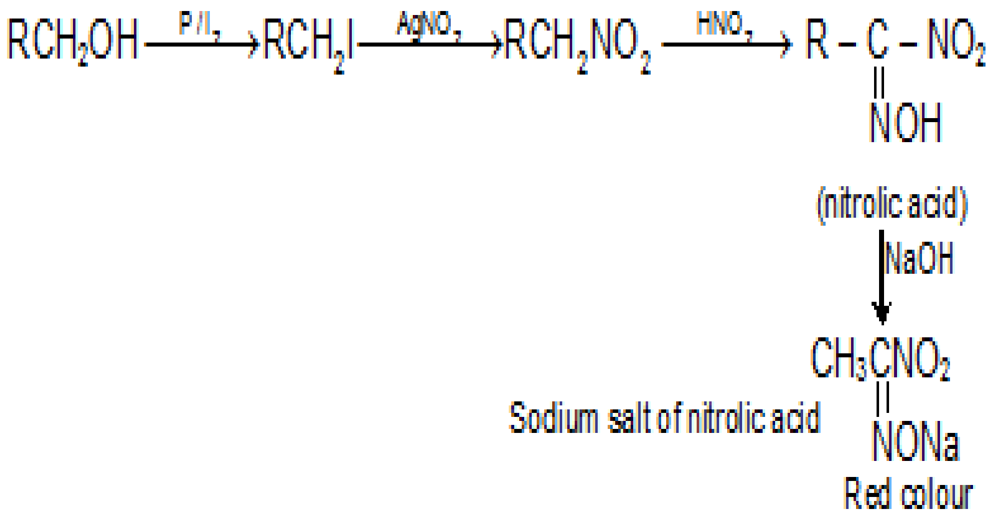
1. Lucas Test:

Alcohols + $ZnCl_2$ + HCl

- 1^o Alcohol: $RCH_2OH + ZnCl_2 + HCl \rightarrow$ No reaction at room temperature
- 2^0 Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5-10 min.
- 3^0 Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ white turbidity instantaneously.

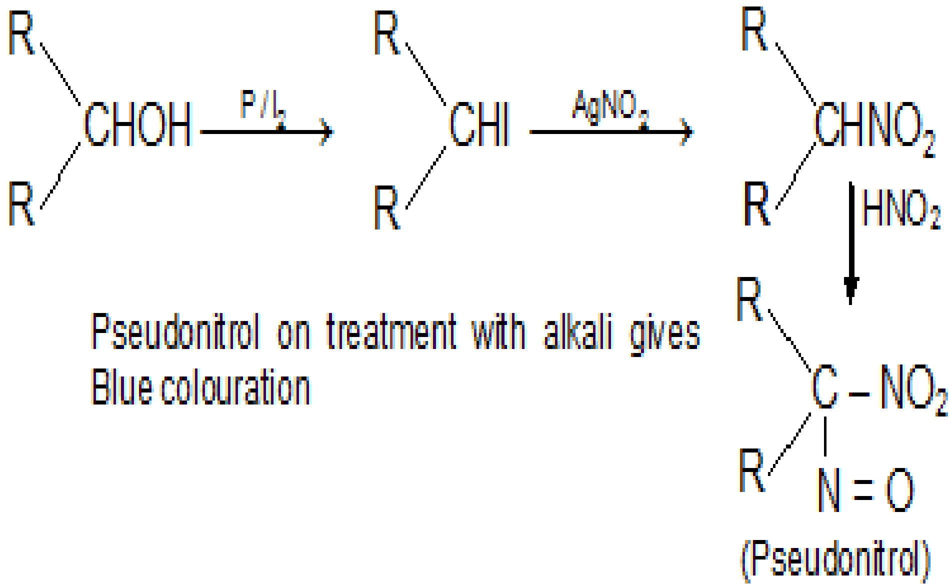
2. Victor Meyer Test

1° alcohol:



Nitrolic acid on treatment with alkali gives colouration

2° alcohol:



Pseudonitrol on treatment with alkali gives Blue colouration

3° alcohol:

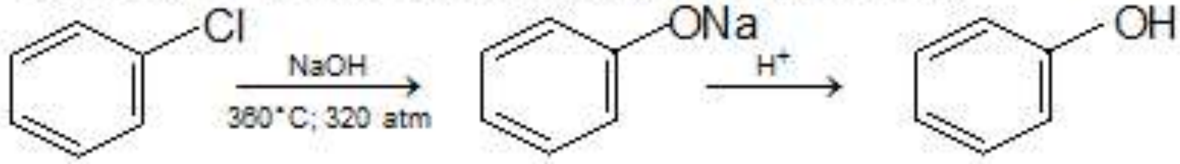
$$R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2} \text{No reaction}$$

(colour less)

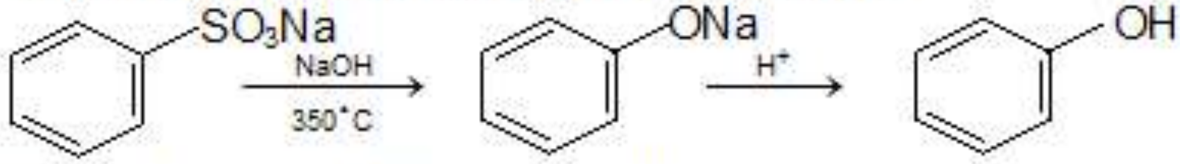
Phenols:

Preparation:

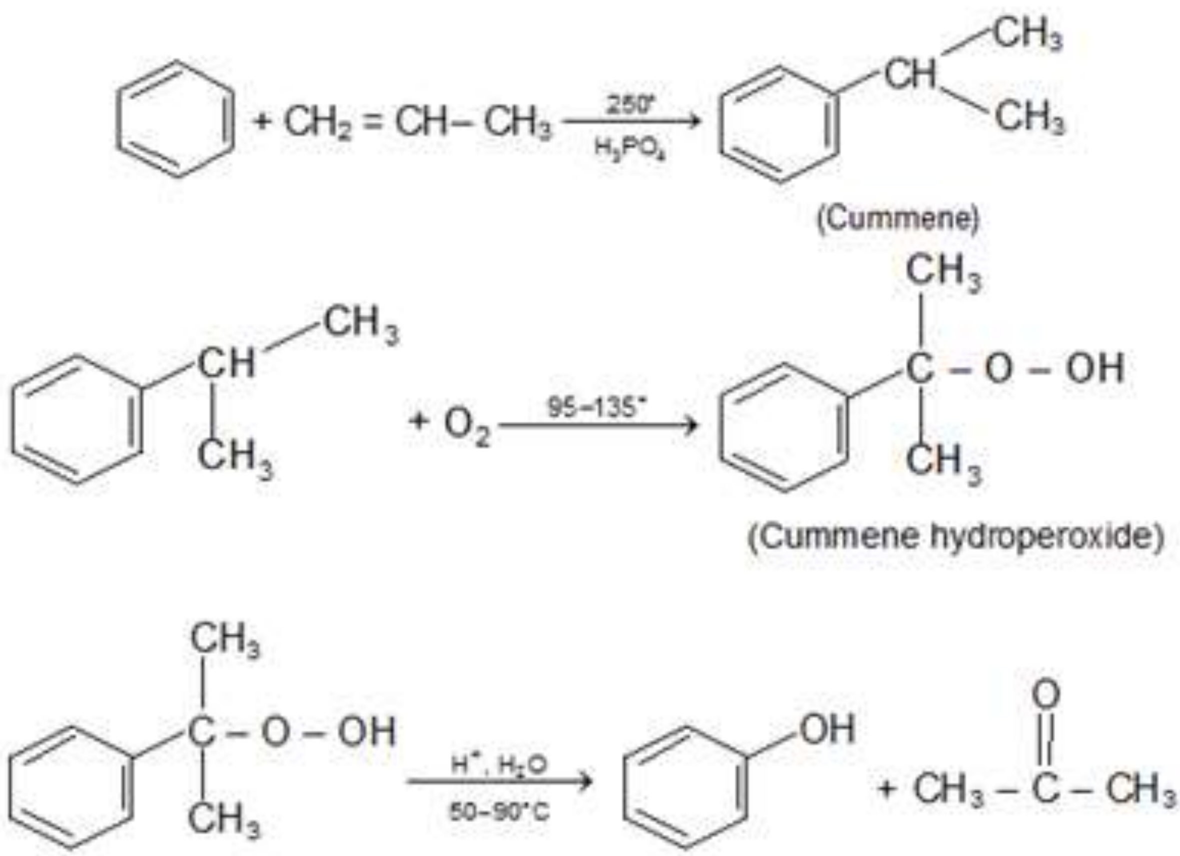
a. **Hydrolysis of chlorobenzene: (Dow's process)**



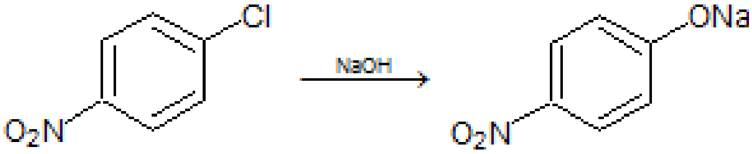
b. **Alkali fusion of Sodium benzene sulfonate**



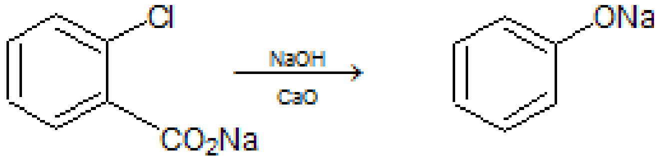
c. **From Cummene Hydroperoxide**



d. **Aromatic Nucleophilic Substitution of Nitro Aryl Halides**



e. **Distillation of phenolic acids with soda-lime produces phenols, e.g. sodium salicylate gives phenol.**



Physical Properties of Phenols

- Phenol is a colorless, toxic, corrosive, needle shaped solid.
- Phenol soon liquifies due to high hygroscopic nature.
- Phenol is less soluble in water, but readily soluble in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is, steam volatile and also is less soluble in water because of intramol ecular hydrogen bonding

Chemical Properties of Phenols

a) Formation of Esters

Phenyl esters (RCOOAr) are not formed directly from RCOOH. Instead, acid chlorides or anhydrides are reacted with ArOH in the presence of strong base

$(CH_3CO)_2O + C_6H_5OH + NaOH \rightarrow CH_3COOC_6H_5 + CH_3COONa + H_2O$

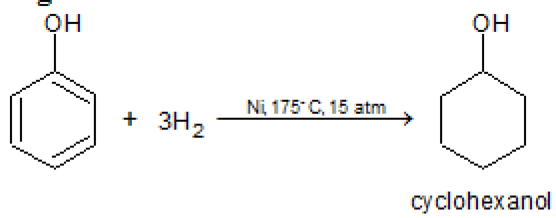
Phenyl acetate

$C_6H_5COCl + C_6H_5OH + NaOH \rightarrow C_6H_5COOC_6H_5 + Na^+Cl^- + H_2O$

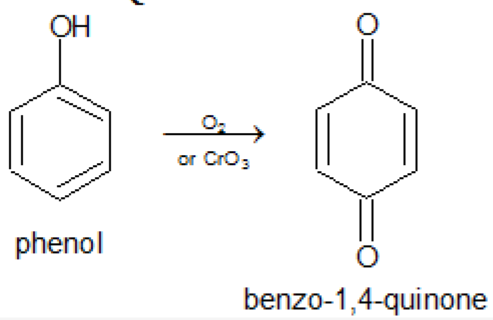
Phenyl benzoate

b) Displacement of OH group: $ArOH + Zn \xrightarrow{\Delta} ArH + ZnO$ (poor yields)

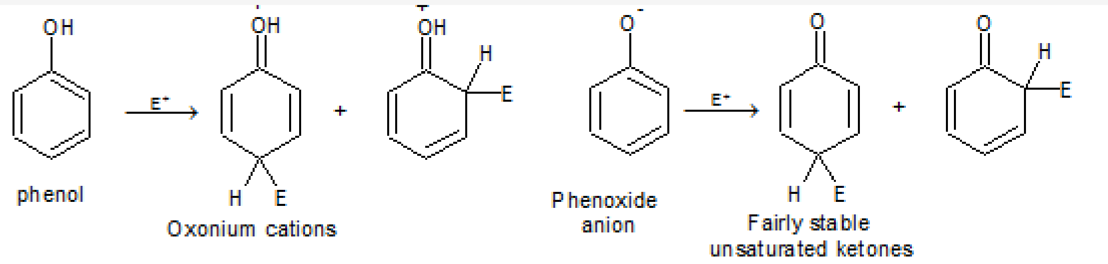
c) Hydrogenation



d) Oxidation to Quionones

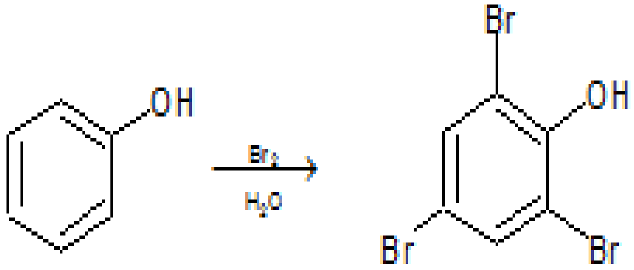


e) Electrophilic Substitution The —OH and even more so the —O(phenoxide) are strongly activating ortho ,para - directing

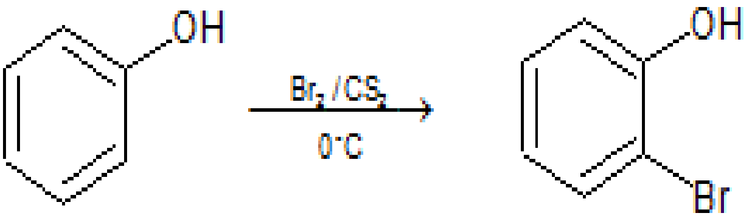


Special mild conditions are needed to achieve electrophilic monosubstituion in phenols because their high reactivity favors both polysubstitution and oxidation

f) Halogenation

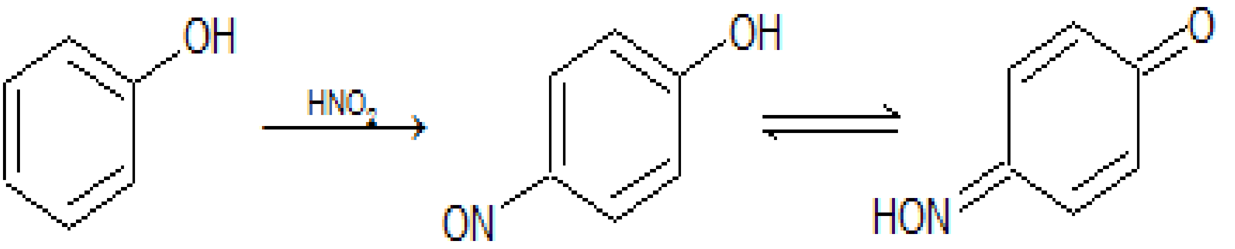


(goes via ArO; no monobromophenols)



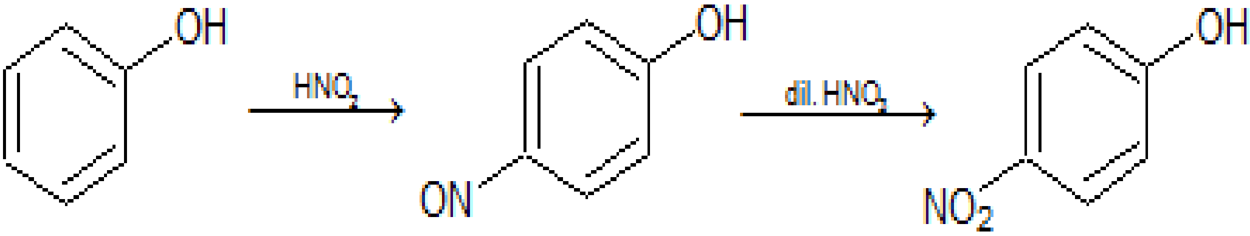
2-bromophenol

h) Nitrosation

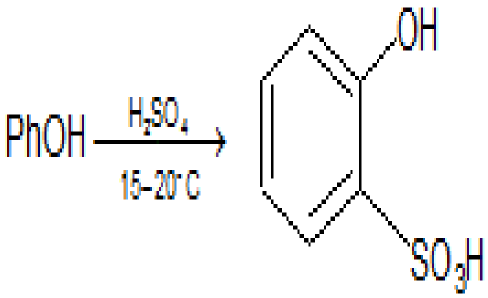


p-nitrosophenol Quinone monoxime

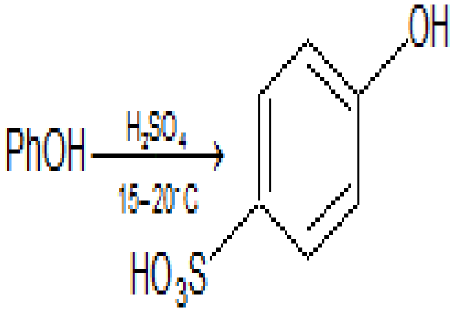
i) Nitration



j) Sulfonation



(rate-controlled)



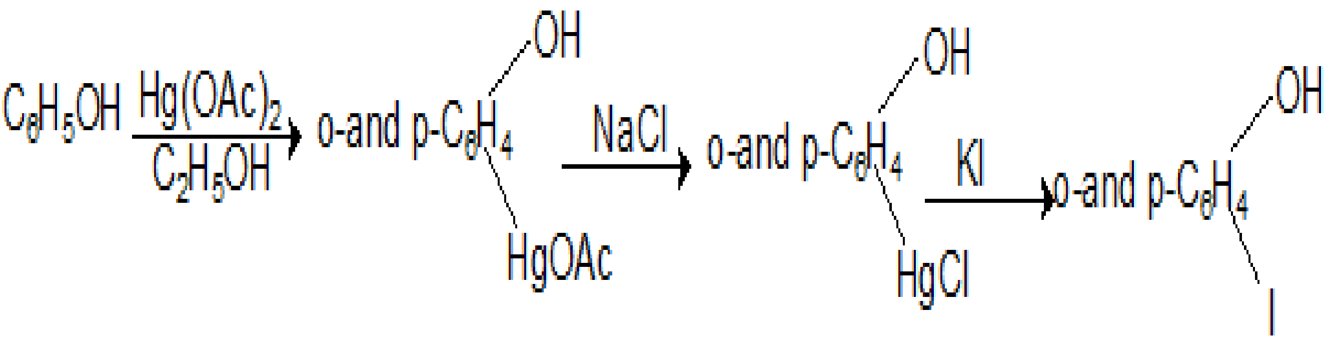
(eqbm-controlled)

k) Diazonium salt coupling to form azophenols

Coupling (G in ArG is an electron – releasing group)

$$ArN_2^+ + C_6H_5G \longrightarrow p\text{-}G - C_6H_4 - N = N - Ar \; (G = OH, NR_2, NHR, NH_2)$$

l) Mercuration



m) Ring alkylation

$$C_6H_5OH + \left\{\begin{matrix} CH_3CH=CH_2 \\ (CH_3)_2CHOH \end{matrix}\right. \xrightarrow[\text{Or HF}]{H_2SO_4} \text{o- and p-}C_6H_4\begin{matrix} OH \\ CH(CH_3)_2 \end{matrix} + H_2O$$

RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O.

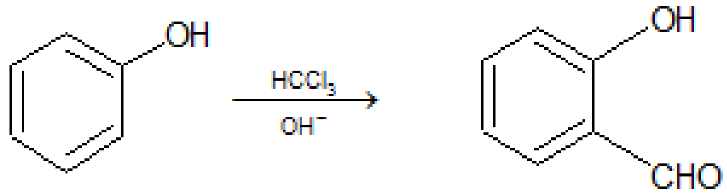
n) Kolbe synthesis of phenolic carboxylic acids

$$C_6H_5ONa + O=C=O \xrightarrow[6\ atm]{125°C} \text{o-}C_6H_4\begin{matrix} OH \\ COONa \end{matrix} \xrightarrow{H_3O^+} \text{o-}C_6H_4\begin{matrix} OH \\ COOH \end{matrix}$$

Sodium salicylate Salicylic acid

Phenoxide carbanion adds at the electrophilic carbon of CO_2, para product is also possible.

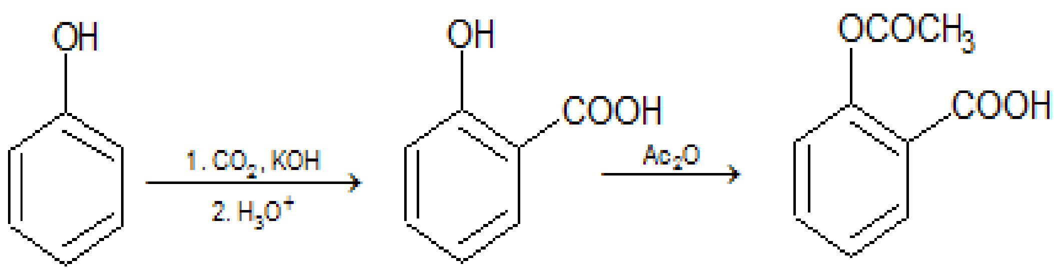
o) Reimer – Tiemann synthesis of phenolic aldehydes



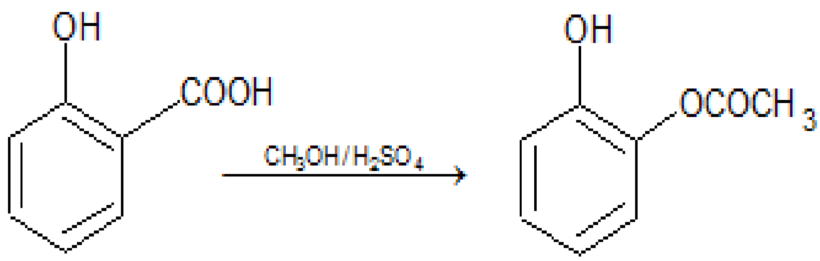
The electrophile is the dichlorocarbene, $:CCl_2$, formation of carbene is an example of α-elimination. $\bar{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)

a)



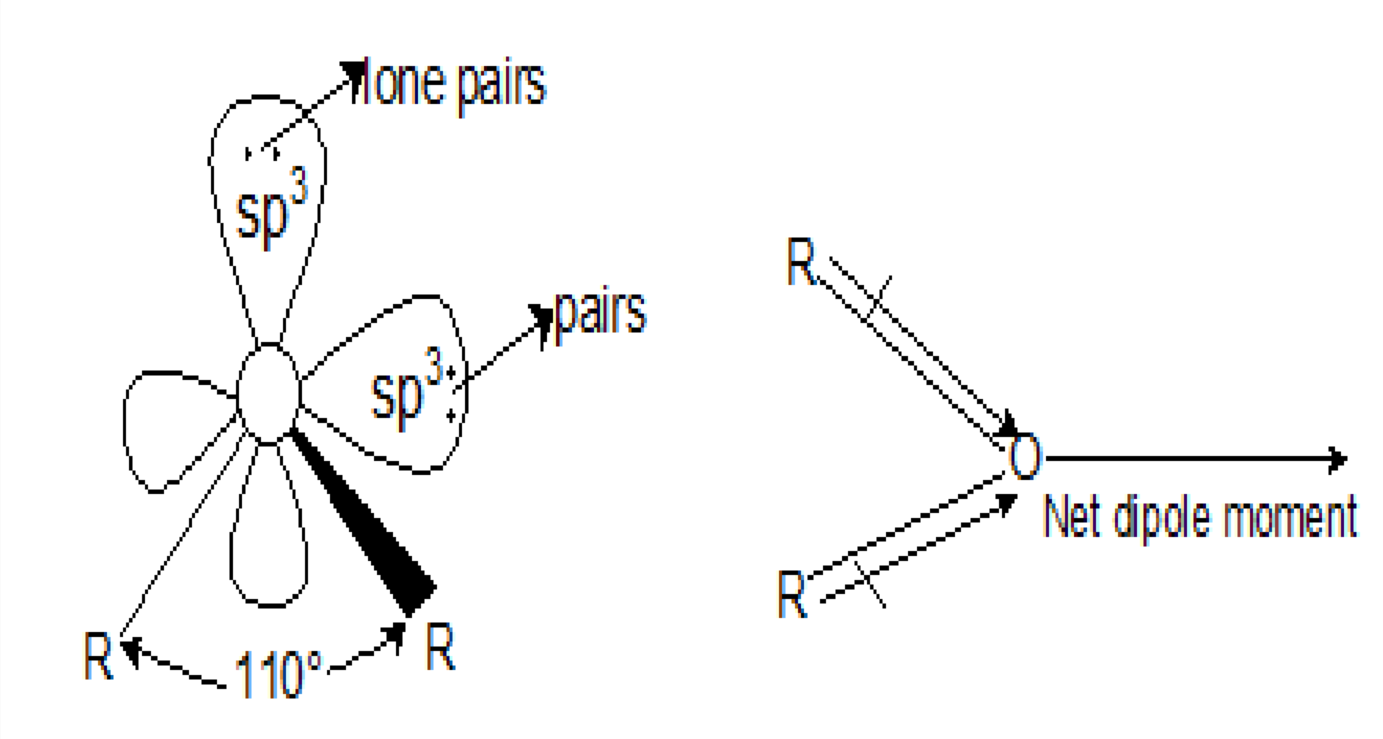
b)



Ethers:

Physical Properties of Ethers

- **Physical state, colour and odour**: Dimethyl ether and ethyl methyl ether is gas at ordinary temperature while the other lower homologues of ethers are colourless liquid with characteristic 'ether smell'.
- **Dipole nature**: Ethers have a tetrahedral geometry i.e., oxygen is sp^3 hybridized. The C— O—C angle in ethers is 110°. Because of the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.



Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

- **Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

Preparation of Ethers:

a) From alcohols:

$$CH_3CH_2OH \xrightarrow[140^0C]{H_2SO_4} \underset{\text{Ether}}{CH_3CH_2-O-CH_2CH_3}$$

Order of dehydration of alcohol leading to formation of ethers: 1° > 2° > 3°

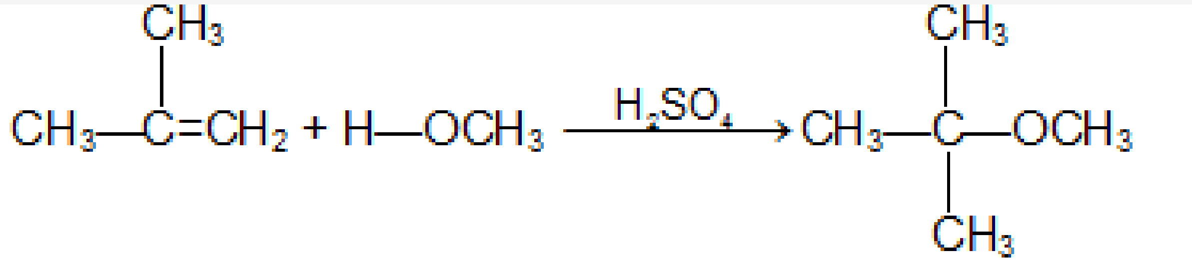
$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2-O-CH_3 + N_2$$

b) Williamson's synthesis:

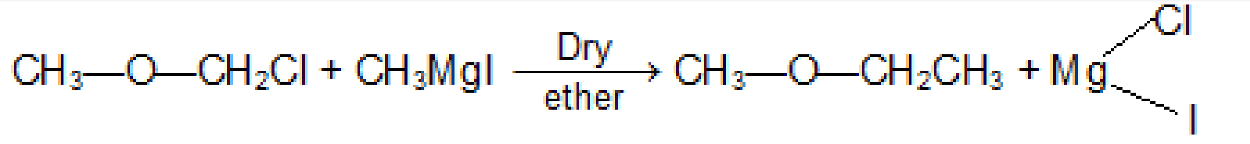
R-X + Na^{+} $^{-}$O-R' → R-O-R' + Na^{+} X^{-}

In case of tertiary substrate elimination occurs giving alkenes.

From alkenes:.



From Grignard reagent: Treating a - halo ethers with suitable Grignard reagents
.

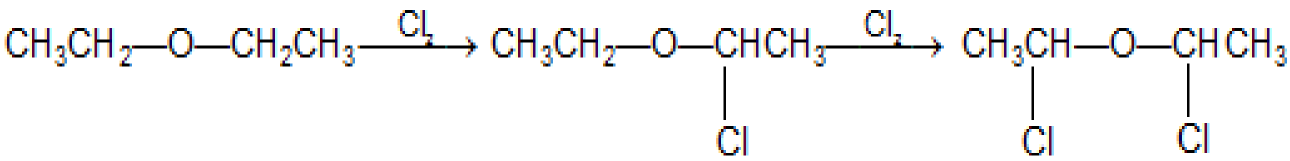


On standing in contact with air, most aliphatic ethers are converted slowly into un stable peroxides. The presence of peroxides is indicated by formation of a red colour w hen the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate
?

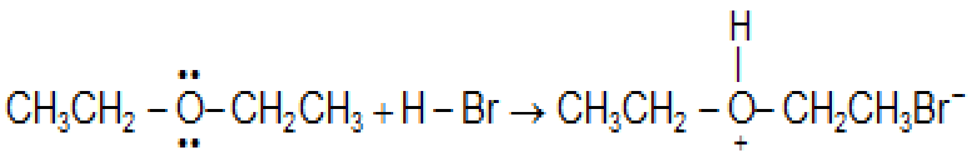
$$\text{Peroxide} + Fe^{2+} \rightarrow Fe^{3+} \xrightarrow{SCN^-} Fe(SCN)_n^{(3-n)-} \ (n = 1 \text{ to } 6)$$

Red

f) Halogenation of ethers:



g) Ethers as base:

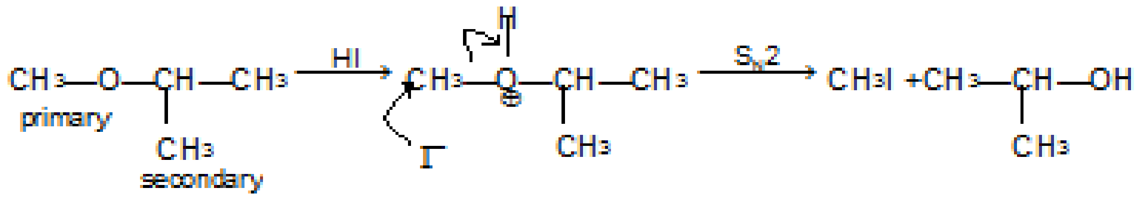
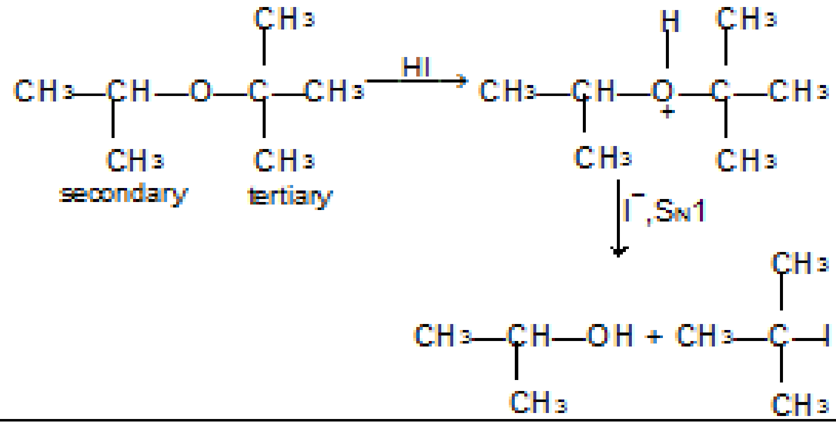
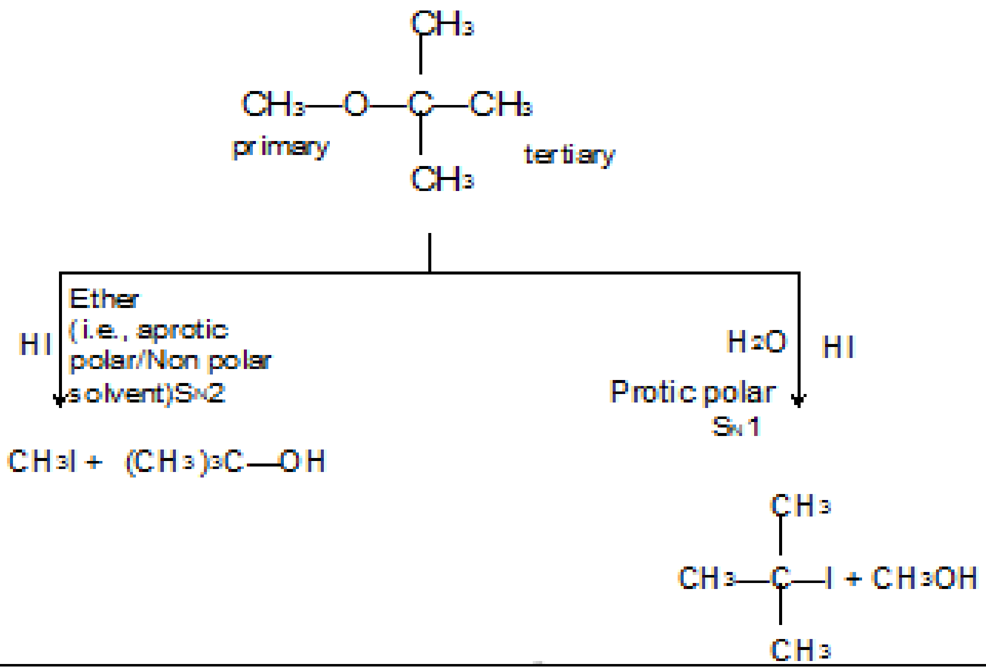
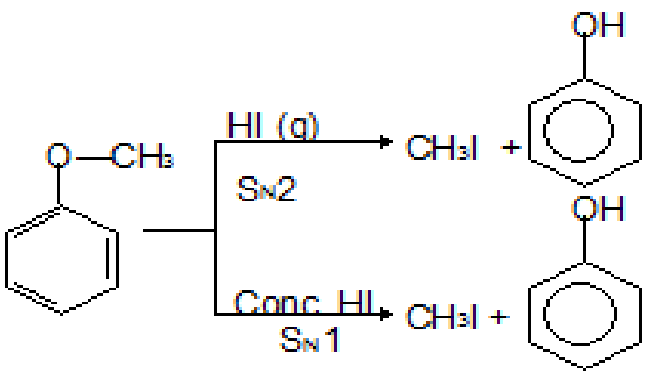


h) Reaction With Cold conc. HI/HBr:

$$R—O—R' + \text{Cold HI} \longrightarrow \text{R-OH} + R'I \ (R' < R)$$

i) Hot conc. HI/HBr:

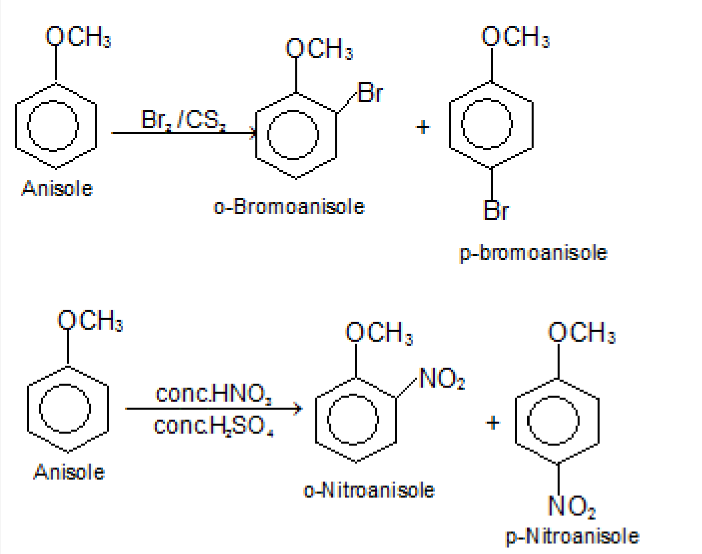
$$R—O—R' + \text{Hot HI} \longrightarrow RI + R'I + H_2O$$

Case I:	
Case II:	
Case III:	
Case IV:	

i) Reaction with acid chlorides and anhydrides:

$$C_2H_5 - O - C_2H_5 + CH_3COCl \xrightarrow[Anhy\ ZnCl_2]{\Delta} C_2H_5Cl + CH_3COOC_2H_5$$

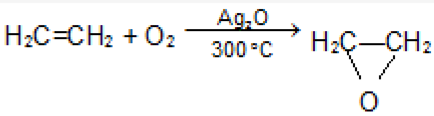
j) Electrophilic substitution reactions



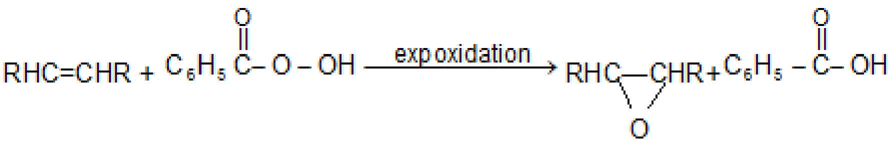
Epoxides or Oxiranes:

Preparation

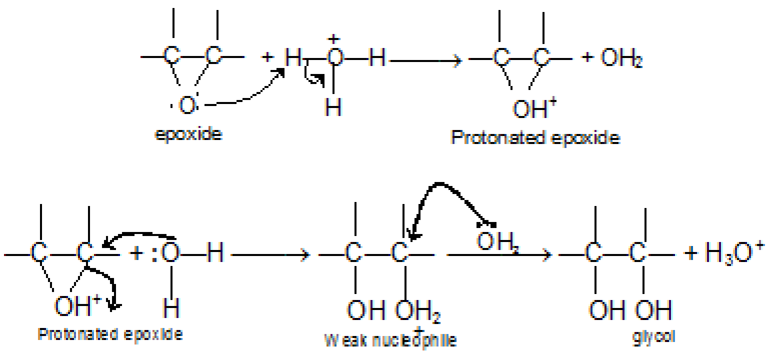
a) Oxidation of ethylene :



b) Expoxidation :



Acid catalysed ring opening



Base catalysed ring opening: