

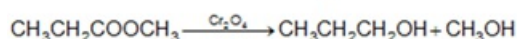
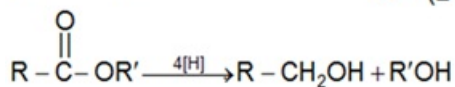
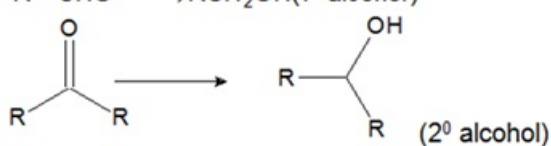
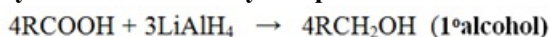
# Revision Notes on Alcohols, Phenols and Ether:

## Alcohols

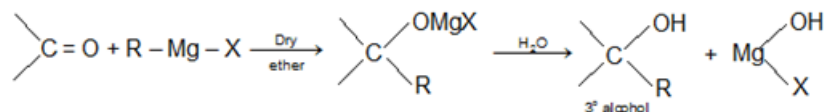
### Preparation of Alcohols:

- By hydrolysis of haloalkanes :  $R-X + \text{aq. KOH} \rightarrow ROH + KX$

- By reduction of Carbonyl compounds

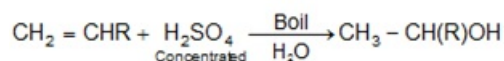


- By the action of Grignard's Reagent on aldehydes, ketones and esters

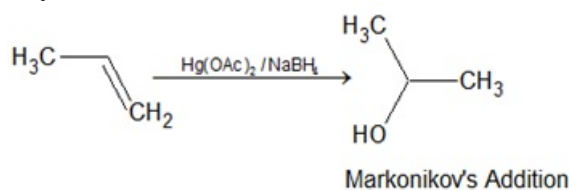


- By Aliphatic Primary Amines:  $RCH_2NH_2 + HNO_2 \rightarrow RCH_2OH + N_2 + H_2O$

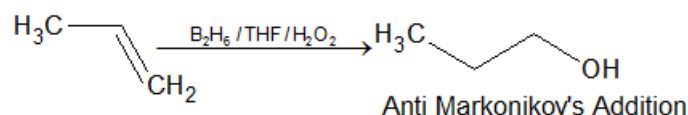
- Hydration of alkenes:



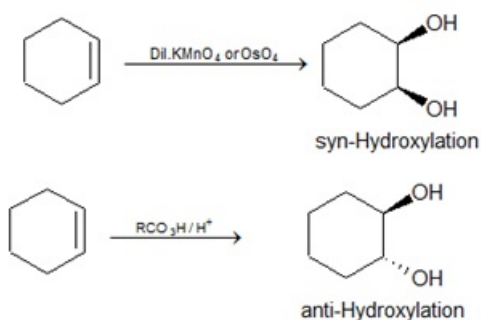
- Oxymercuration-demercuration:



- Hydroboration-oxidation:



- Hydroxylation of alkenes:

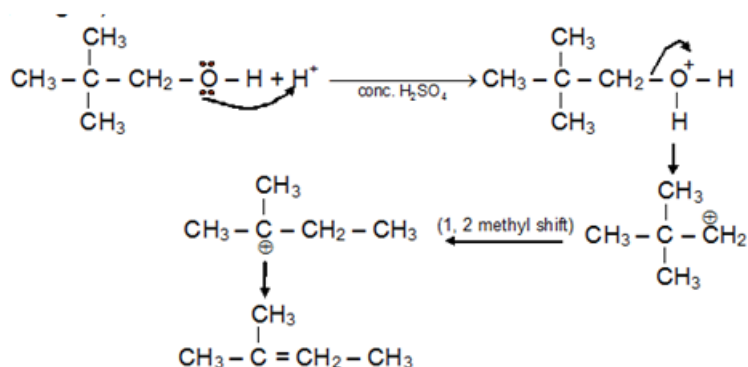


### Physical Properties of Alcohol:

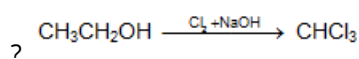
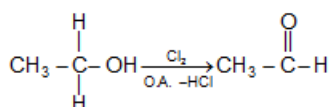
- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular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

### Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:**  $\text{ROH} + \text{Na} \rightarrow 2\text{RO}^+\text{Na}^- + \text{H}_2$
- **Formation of Halides:**
  - $3\text{ROH} + \text{P} + \text{I}_2 \rightarrow 3\text{RI} + \text{H}_3\text{PO}_3$
  - $\text{ROH} + \text{SOCl}_2 / \text{PCl}_3 / \text{PCl}_5 \rightarrow \text{RCl}$
  - $\text{ROH} + \text{HX} \rightarrow \text{RX}$
  - $\text{ROH} + \text{NaBr}, \text{H}_2\text{SO}_4 \rightarrow \text{R-Br}$
  - $\text{ROH} + \text{Zn} + \text{HCl} \rightarrow \text{R-Cl}$
  - $\text{R}_2\text{C-OH alcohol} + \text{HCl} \rightarrow \text{R}_2\text{CCl}$
- **Reaction with  $\text{HNO}_3$ :**  $\text{R-OH} + \text{HO-NO}_2 \rightarrow \text{R-O-NO}_2$
- **Reaction with carboxylic acid (Esterification) :**  $\text{R-OH} + \text{R'-COOH} + \text{H}^+ \rightarrow \text{R'-COOR}$
- **Reaction with Grignard reagent:**  $\text{R'OH} + \text{RMgX} \rightarrow \text{RH} + \text{R'OMgX}$
- **Reduction of alcohol :**  $\text{ROH} + 2\text{HI} + \text{Red P} \rightarrow \text{RH} + \text{I}_2 + \text{H}_2\text{O}$
- **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:  $3^\circ > 2^\circ > 1^\circ$
- **Satzeff's Rule :** Elimination through  $\beta$  carbon containing minimum  $\beta$  hydrogen



- Oxidation of Alcohol:**  
 $\text{RCH}_2\text{-OH} + [\text{O}] \rightarrow \text{RCHO} \rightarrow \text{RCOOH}$   
 $\text{RCH}_2\text{-OH} + [\text{O}] + \text{PCC} \rightarrow \text{RCHO}$
- Haloform Reaction:** Compound containing  $\text{CH}_3\text{CO-}$  group (or compound on oxidation gives  $\text{CH}_3\text{CO-}$  group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.  $\text{CH}_3\text{-CH}_2\text{-COCH}_2\text{-CH}_3$ ,  $\text{CH}_3\text{-CO-Cl}$ ,  $\text{CH}_3\text{COOH}$  will not respond to haloform reaction while  $\text{CH}_3\text{CH}_2\text{OH}$  will respond to haloform Reaction.



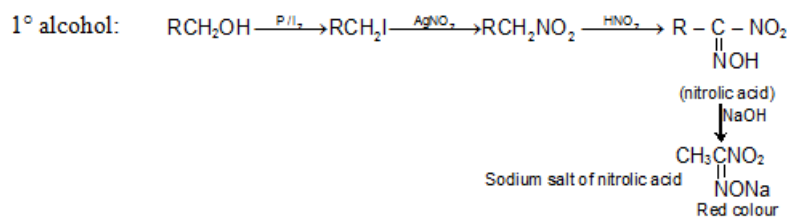
### Test for Alcohols:

#### 1. Lucas Test:

Alcohols +  $\text{ZnCl}_2$  +  $\text{HCl}$

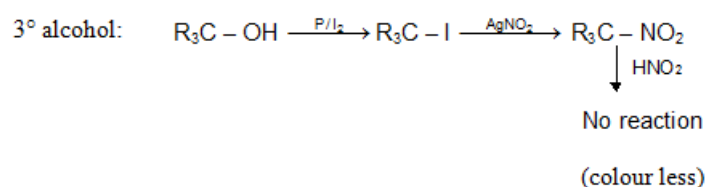
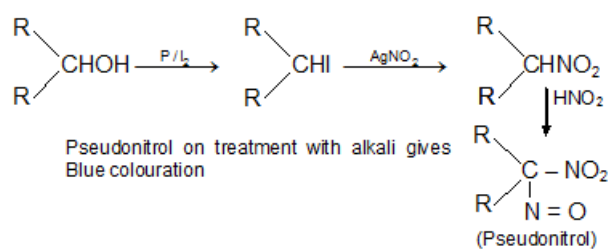
- 1° Alcohol:  $\text{RCH}_2\text{OH} + \text{ZnCl}_2 + \text{HCl} \rightarrow$  No reaction at room temperature
- 2° Alcohol:  $\text{R}_2\text{CHOH} + \text{ZnCl}_2 + \text{HCl} \rightarrow \text{R}_2\text{CHCl}$  White turbidity after 5-10 min.
- 3° Alcohol:  $\text{R}_3\text{CHOH} + \text{ZnCl}_2 + \text{HCl} \rightarrow \text{R}_3\text{CHCl}$  white turbidity instantaneously.

#### 2. Victor Meyer Test



Nitrolic acid on treatment with alkali gives colouration

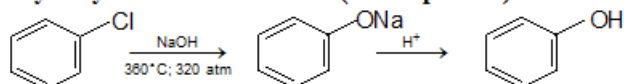
2° alcohol:



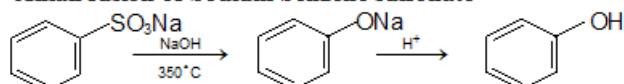
## Phenols:

### Preparation:

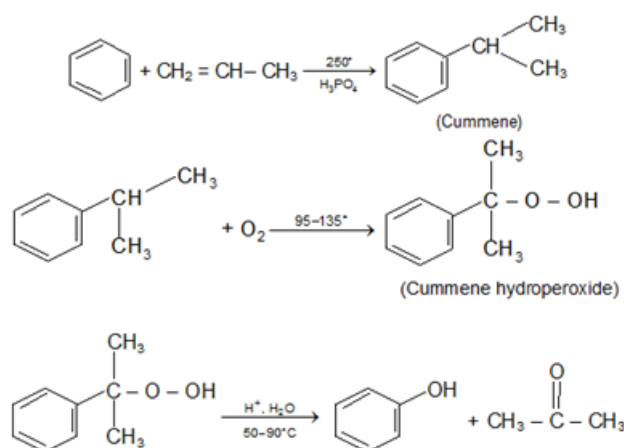
#### a. Hydrolysis of chlorobenzene: (Dow's process)



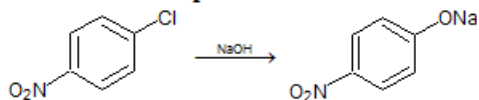
#### b. Alkali fusion of Sodium benzene sulfonate



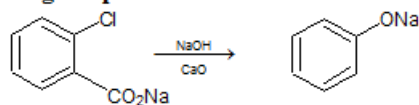
#### c. From Cumene Hydroperoxide



**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 intramolecular hydrogen bonding

**Chemical Properties of Phenols**

**a) Formation of Esters**

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



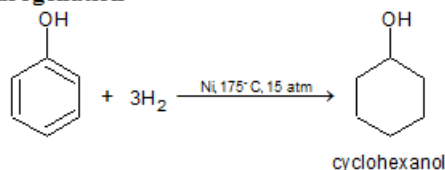
Phenyl acetate



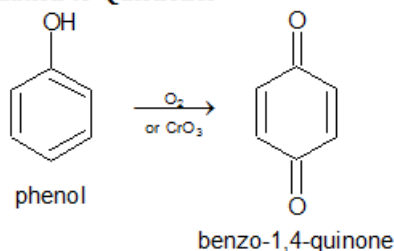
Phenyl benzoate

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

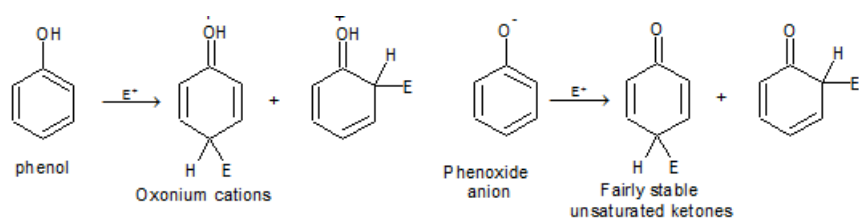
**c) Hydrogenation**



**d) Oxidation to Quinones**

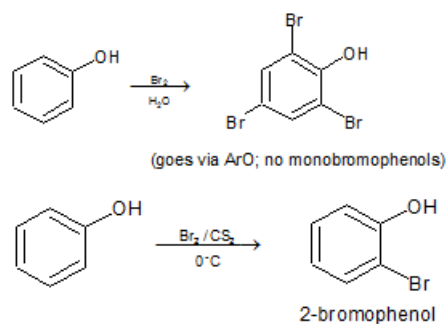


**e) Electrophilic Substitution** The  $\text{—OH}$  and even more so the  $\text{—O(phenoxide)}$  are strongly activating ortho, para - directing

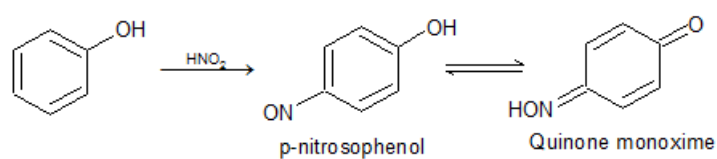


Special mild conditions are needed to achieve electrophilic monosubstitution in phenols because their high reactivity favors both polysubstitution and oxidation

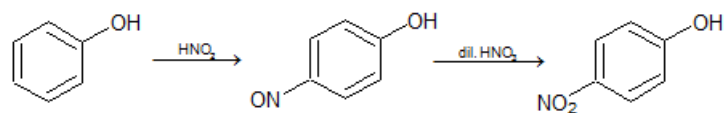
#### f) Halogenation



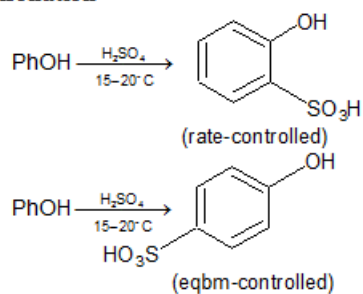
#### h) Nitrosation



#### i) Nitration

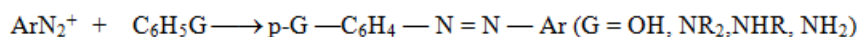


**j) Sulfonation**

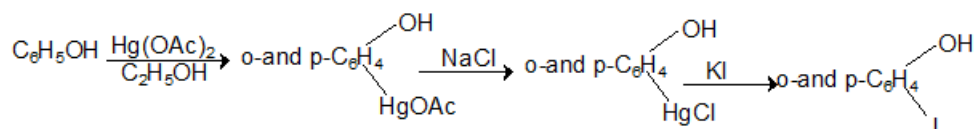


**k) Diazonium salt coupling to form azophenols**

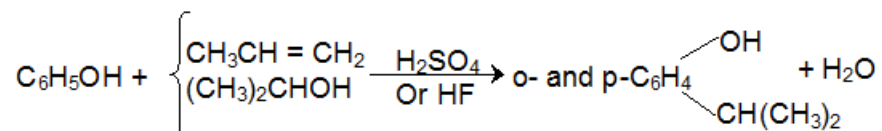
**Coupling** (G in ArG is an electron – releasing group)



**l) Mercuration**

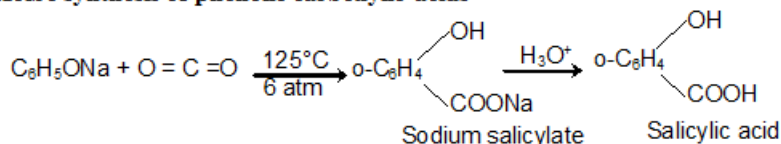


**m) Ring alkylation**



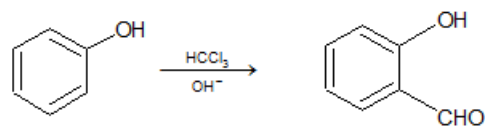
RX and  $\text{AlCl}_3$  give poor yields because  $\text{AlCl}_3$  coordinates with O.

**n) Kolbe synthesis of phenolic carboxylic acids**



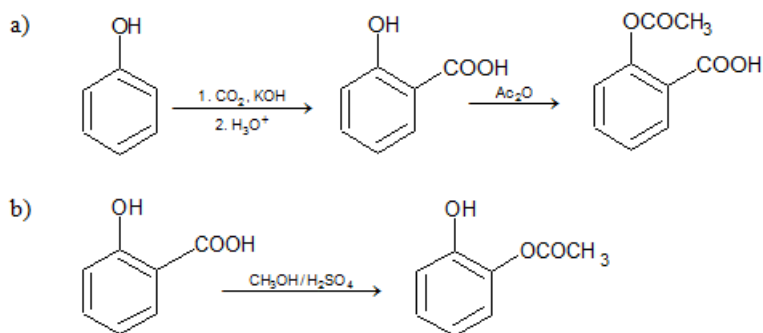
Phenoxide carbanion adds at the electrophilic carbon of  $\text{CO}_2$ , para product is also possible.

**o) Reimer – Tiemann synthesis of phenolic aldehydes**



The electrophile is the dichlorocarbene,  $\text{CCl}_2$ , formation of carbene is an example of  $\alpha$ -elimination.  $\text{OH}^- + \text{HCCl}_3 \xrightarrow{-\text{HCl}} \text{:CCl}_2$

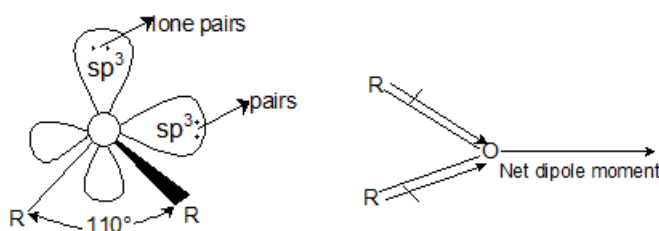
p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)



## 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  $110^\circ$ . 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  $110^\circ$ , resulting in a net dipole moment.

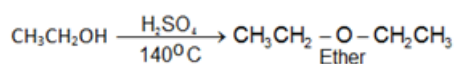


Bond angle of ether is greater than that of tetrahedral bond angle of  $109^\circ 28'$ .

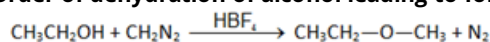
- Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

### Preparation of Ethers:

a) From alcohols:



Order of dehydration of alcohol leading to formation of ethers:  $1^\circ > 2^\circ > 3^\circ$



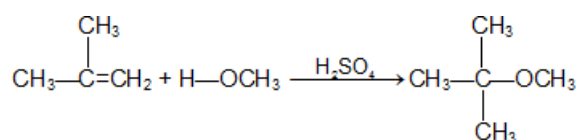
b) Williamson's synthesis:



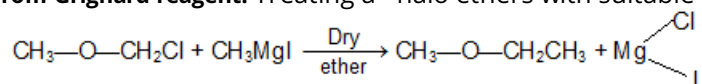
In case of tertiary substrate elimination occurs giving alkenes.

From alkenes:.

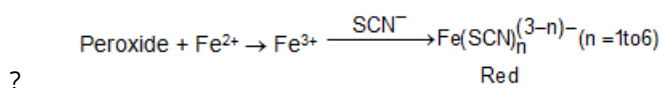




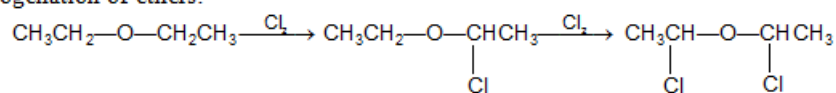
**From Grignard reagent:** Treating a - halo ethers with suitable Grignard reagents.



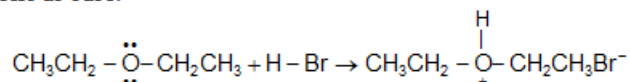
On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate



f) Halogenation of ethers:



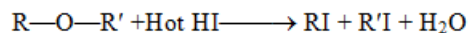
g) Ethers as base:



h) Reaction With Cold conc. HI/HBr:

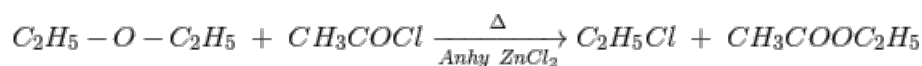


i) Hot conc. HI/HBr:

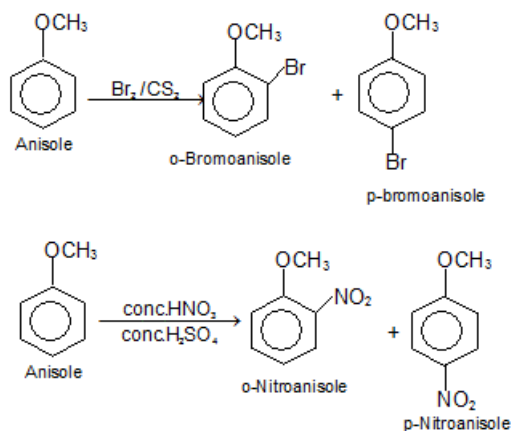


<b>Case I:</b>	<p> <math>\text{CH}_3\text{-O-CH(CH}_3\text{)-CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{-O}^+\text{(H)-CH(CH}_3\text{)-CH}_3 \xrightarrow{\text{I}^-} \text{CH}_3\text{I} + \text{CH}_3\text{-CH(CH}_3\text{)-OH}</math> </p> <p>primary      secondary</p>
<b>Case II:</b>	<p> <math>\text{CH}_3\text{-CH(CH}_3\text{)-O-C(CH}_3\text{)}_2\text{-CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{-CH(CH}_3\text{)-O}^+\text{(H)-C(CH}_3\text{)}_2\text{-CH}_3 \xrightarrow{\text{I}^-} \text{CH}_3\text{-CH(CH}_3\text{)-OH} + \text{CH}_3\text{-C(CH}_3\text{)}_2\text{-I}</math> </p> <p>secondary      tertiary</p>
<b>Case III:</b>	<p> <math>\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Ether (i.e., aprotic polar/Non polar solvent) } S_N2]{\text{HI}} \text{CH}_3\text{I} + (\text{CH}_3)_3\text{C-OH}</math> </p> <p>primary      tertiary</p> <p> <math>\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Protic polar } S_N1]{\text{H}_2\text{O, HI}} (\text{CH}_3)_3\text{C-I} + \text{CH}_3\text{OH}</math> </p>
<b>Case IV:</b>	<p> <math>\text{C}_6\text{H}_5\text{OCH}_3 \xrightarrow[\text{S}_N2]{\text{HI (g)}} \text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{OH}</math> </p> <p> <math>\text{C}_6\text{H}_5\text{OCH}_3 \xrightarrow[\text{S}_N1]{\text{Conc. HI}} \text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{OH}</math> </p>

#### i) Reaction with acid chlorides and anhydrides:



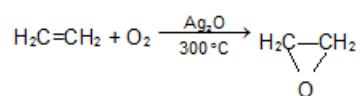
#### j) Electrophilic substitution reactions



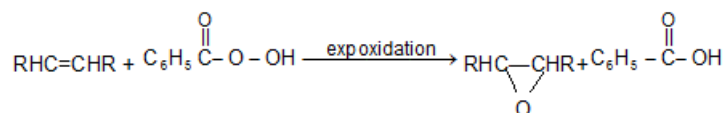
#### Expoxides or Oxiranes:

## Preparation

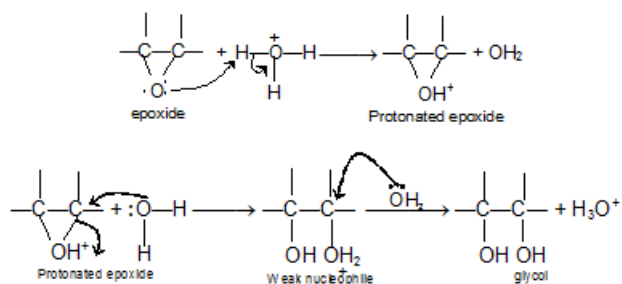
### a) Oxidation of ethylene :



### b) Epoxidation :



### Acid catalysed ring opening



### Base catalysed ring opening:

