MIND MAP

Alcohol

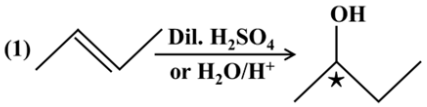
General Methods of Preparation

From Alkenes

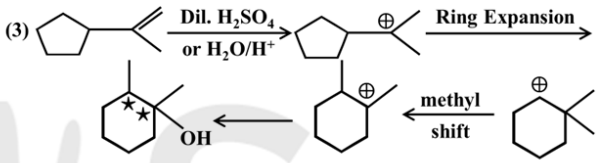
1. By Hydration

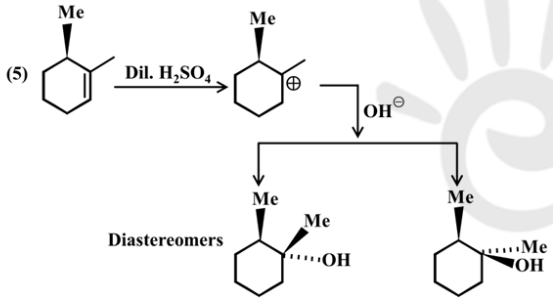
$$CH_3-CH=CH_2 \xrightarrow[H_2O]{H^{\oplus}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2$$

Carbocation intermediate so rearrangement is possible.

(1) 

Racemic mixture

(3) 

(5) 

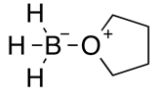
2. By Hydroboration Oxidation (HBO)

Takes place by Anti Markovnikov Rule in presence of H2O2 without Carbocation Rearrangement.

$$CH_3-CH=CH_2 \xrightarrow[(ii)\ H_2O_2/HO^-]{(i)\ B_2H_6/THF} CH_3-CH_2-\underset{\underset{OH}{|}}{CH_2}$$

(1° alcohol)

$$\underset{B_2H_6}{THF} \rightarrow BH_3 + BH_3$$

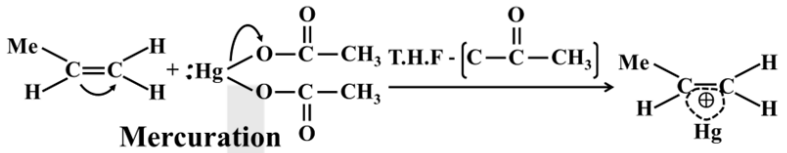


3. By Oxymercuration Demercuration (OMDM)

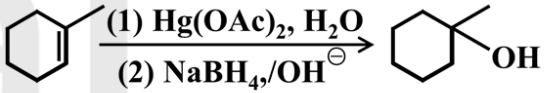
Takes place by Markovnikov rule.

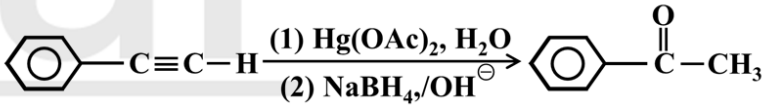
No carbocation is formed during reaction hence no rearrangement takes place.

$$CH_3-CH=CH_2 \xrightarrow[(ii)\ NaBH_4,\ HO^-]{(i)\ Hg(OAc)_2,\ H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$



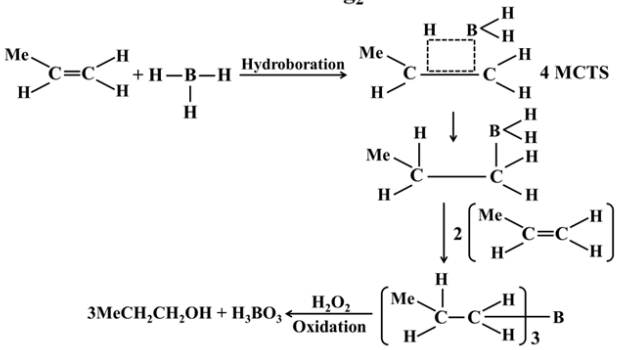
Mercuration

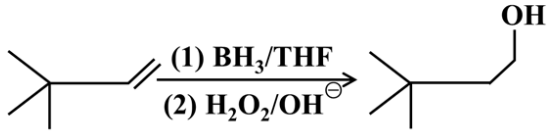
(1) 

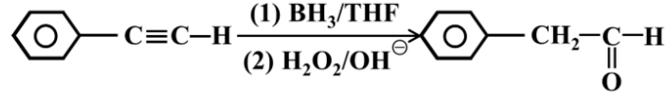
(2) 

4. From Alkyl Halides (By Hydrolysis)

$$CH_3-CH_2-Cl \xrightarrow[or\ Moist\ Ag_2O]{Aq.\ KOH} CH_3CH_2-OH$$



(1) 

(2) 

MIND MAP

Alcohol

From Ethers

$$R-O-R \xrightarrow{\text{Dil. } H_2SO_4} R-OH + R-OH$$

$$R-O-R \xrightarrow[S_N1]{\text{Dil.}H_2SO_4} R-OH + R-OH$$

From Hydrolysis of Ester

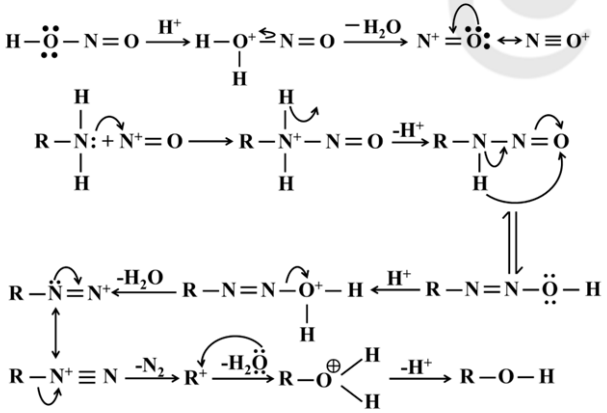
$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-OH + R'OH$$

From Primary Amines(conversion of 1 degree amine into RN2+)

$$R-NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2 + HCl} R-OH + N_2 + H_2O$$

Mechanism

$$NaNO_2 + HCl \longrightarrow H-O-N=O + NaCl$$

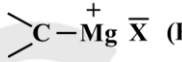


Carbocation intermediate is formed so rearrangement is possible.

Grignard Reagent RMgX

Organometallic Compounds

Organometallic compounds are the organic compounds in which a metal atom is directly attached to carbon of organic molecules through covalent bond or ionic bond.



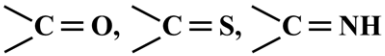
Preparation of Grignard Reagent

$$RX + Mg \xrightarrow[\text{Ether}]{\text{Dry and pure}} RMgX$$

Ether is used as a solvent because it is a Lewis Base that coordinates its lone pair of electrons to electron-deficient magnesium atom, therefore providing stability to the Grignard Reagent.

Reactions of Grignard Reagents

Grignard reagents form adducts by addition on the following types of pi bonds.



Synthesis of Alkanes

With compounds having reactive hydrogen atom (Acid – Base Reaction).

General Reactions

$$R-MgX + H-Z \longrightarrow R-H + ZMgX$$

$$CH_3-MgX + H-OH \longrightarrow CH_3-H + Mg(OH)X$$

$$C_2H_5-MgX + H-OR \longrightarrow C_2H_5-H + Mg(OR)X$$

$$C_3H_7-MgX + H-OC_6H_5 \longrightarrow C_3H_7-H + Mg(OC_6H_5)X$$

With Alkyl Halide (Coupling)

$$R-MgX + X'-R' \longrightarrow R-R' + MgXX'$$

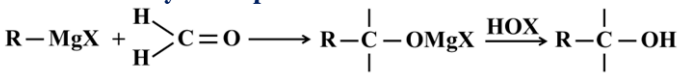
(B) Synthesis of Alkenes

$$R-MgX + X'-CH_2-CH=CH_2 \longrightarrow R-CH_2-CH=CH_2 + MgXX'$$

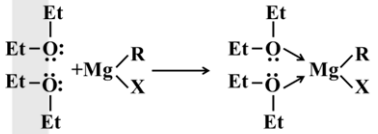
Allyl halide

Synthesis of Alcohols from Grignard Reagent

From Carbonyl Compounds



This is nucleophilic addition reaction.



Alkylmagnesium halide diethetate

The reaction is used for estimation of reactive hydrogen atoms present in a molecule.

This method is called Zerewitinoff's method of estimation of reactive hydrogen atoms.

$$C_2H_5-MgX + H-NH_2 \longrightarrow C_2H_5-H + Mg(NH_2)X$$

$$C_2H_5-MgX + H-SR \longrightarrow C_2H_5-H + Mg(SR)X$$

$$C_2H_5-MgX + H-C\equiv N \longrightarrow CH_3-H + Mg(CN)X$$

$$C_2H_5-MgX + H-C\equiv CH \longrightarrow C_2H_5-H + HC\equiv C-MgX$$

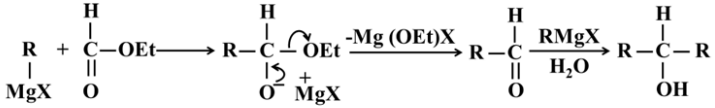
(Ethynylmagnesium halide)

MIND MAP

Alcohol

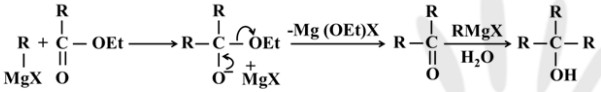
From Acid Derivative

Secondary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard Reagent and adding formic ester to it.

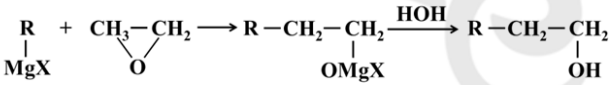


Nucleophilic addition elimination reaction S_NAE

Tertiary alcohols are obtained on hydrolysis of the product obtained by taking excess of Grignard reagent and an ester of a higher homologue of formic acid.



From Epoxides

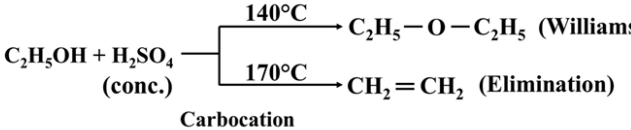


Oxirane

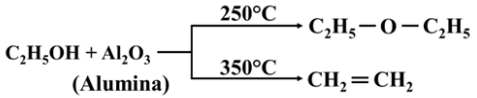
Chemical Properties of Alcohols

(i) Dehydration: Removal of H2O by two type

(a) Intermolecular removal of H2O [forms ether]
(b) Intramolecular removal of H2O [forms alkene]



Carbocation intermediate



Ease of dehydration follows the order 3° ROH > 2° ROH > 1° ROH > CH3OH

Test of Alcohols (1) Lucas Test

A mixture of HCl(conc.) and anhydrous ZnCl2 is called Lucas reagent.

p-alcohol $\xrightarrow{ZnCl_2 + HCl}$ No turbidity at room temp. [on heating within 30 minutes.]

s-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 5 minutes

t-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 1 minutes

This test is used to differentiate 1°, 2° and 3° alcohols.

(2) Victor - Meyer Test(RBC Test)

This is a colour test for alcohols (primary, secondary & tertiary).

p-alcohol → Red colour
s-alcohol → Blue colour
t-alcohol → No colour

This test is used to differentiate 1°, 2° and 3° alcohols.

Dichromate Test

$1° \text{ Alcohol} \xrightarrow[\text{Orange } [Cr^{+6}]]{H^{\oplus}/\ K_2Cr_2O_7} \text{Acid} + Cr^{+3}$ [green]

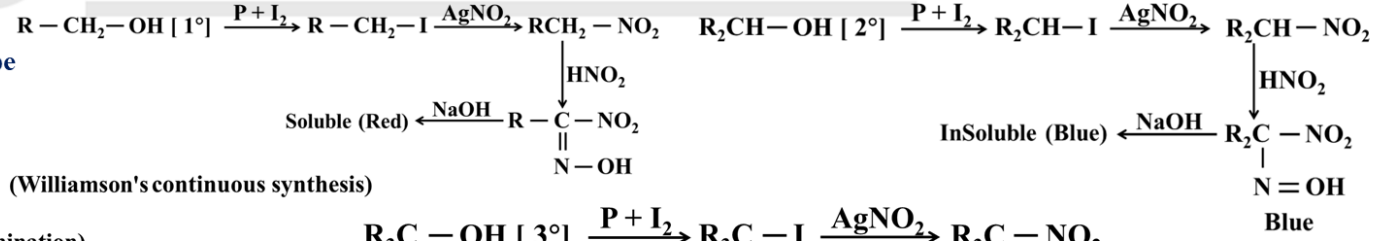
$2° \text{ Alcohol} \xrightarrow[\text{Orange } [Cr^{+6}]]{H^{\oplus}/\ K_2Cr_2O_7} \text{Ketone} + Cr^{+3}$ [green]

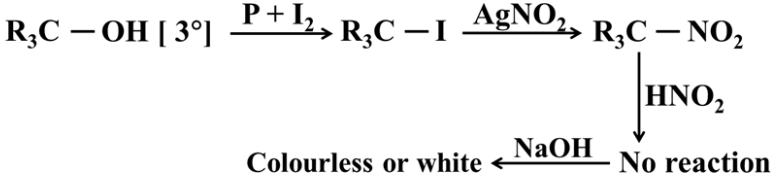
$3° \text{ Alcohol} \xrightarrow[\text{Orange } [Cr^{+6}]]{H^{\oplus}/\ K_2Cr_2O_7}$ No Oxidation, no Green

(b) Test of Alcholic Group

$R-OH \xrightarrow{Na} R-ONa + \frac{1}{2}H_2$ [effervesence of H_2]

$R-OH \xrightarrow{PCl_5} R-Cl + POCl_3 + HCl \xrightarrow{NH_3} NH_4Cl$ [White fumes]



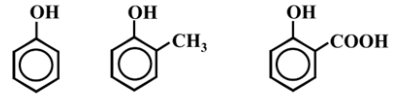


MIND MAP

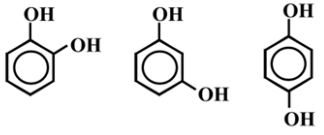
Phenol

Phenolic Compounds

Compounds in which -OH group is directly attached to sp^2 carbon of benzene ring.



Phenol O – cresol Salicylic acid



catechol resorcinol quinol

General Methods of Preparation

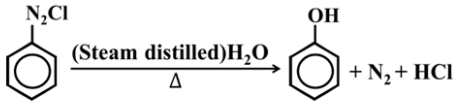
From Benzene Sulphonic Acid

When Sodium salt of Benzene Sulphonic Acid is fused with NaOH, Phenol is obtained.

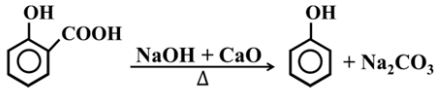
$$C_6H_5SO_3Na \xrightarrow[(ii)\ H^+]{(i)\ NaOH/\Delta} C_6H_5OH + Na_2SO_3$$

From Benzene Diazonium Chloride

When Benzene Diazonium Chloride solution is warmed, Phenol is obtained with evolution of Nitrogen.



By Distilling A Phenolic Acid With Sodalime (Decarboxylation)



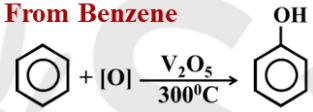
Salicylic acid

From Grignard Reagent

The Grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol.

$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

From Benzene



From Chloro Benzene

$$Ph-Cl \xrightarrow{Aq.\ NaOH} \text{No nucleophilic substitution at normal condition}$$

Stable By Resonance

$$R-Cl \xrightarrow{Aq.\ NaOH} R-OH\ [NSR] \qquad Ph-Cl \xrightarrow[623\ K]{Aq.\ NaOH} Ph-OH$$

Industrial Preparation of Phenol

Phenol Can Be Prepared Commercially By

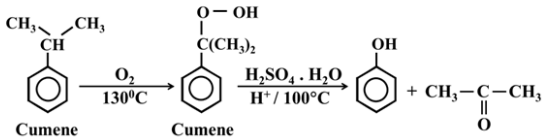
(a) Cumene

(b) Dow's process

From Cumene (Isopropyl Benzene)

Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst.

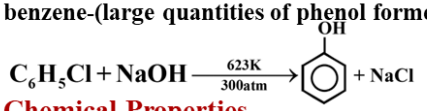
This is decomposed by dil. H2SO4 into phenol and acetone.



Cumene Cumene hydroperoxide

Dow Process

This process involves alkaline hydrolysis of chloro benzene-(large quantities of phenol formed).



Chemical Properties

(A) Reactions due to –OH group

Acidic Nature

Phenol is a weak acid.

The acidic nature of phenol due to formation of stable phenoxide ion in solution.

The phenoxide ion is stable due to resonance.

Reaction with PCl5

Phenol reacts with PCl_5 to form chloro benzene.

The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

Reaction with Zn Dust

When phenol is distilled with Zinc dust benzene is obtained.

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

Reaction with $FeCl_3$

Phenol gives violet colouration with $FeCl_3$ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow \text{Voilet colour}$$

This reaction is used to differentiate phenol from alcohols.

Acetylation (Schotten-Baumann Reaction)

Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

$$C_6H_5OH + ClCOCH_3 \xrightarrow[-HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-CH_3$$

MIND MAP

Phenol

Ether Formation (Alkylation)

Phenol reacts with alkyl halides in alkali solution to form phenyl ethers. (Williamson's synthesis)

$C_6H_5OH + NaOH \xrightarrow{\text{Alkali solution}} C_6H_5ONa \xrightarrow[-NaX]{RX} C_6H_5OR$

Sodium Phenoxide

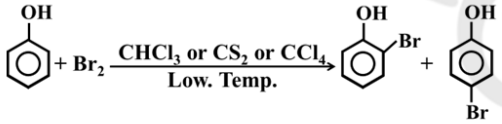
(B) Reaction of Benzene Ring

The —OH group is ortho and para directing.

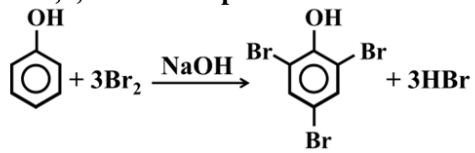
It activates the benzene molecule.

Halogenation

Phenol reacts with Bromine in CCl_4 to form mixture of ortho and para bromo phenol.

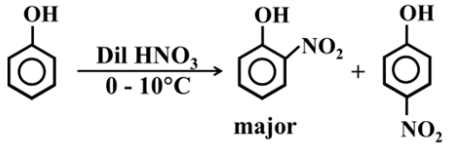


Phenol reacts with bromine water to form a white ppt. of 2,4,6 tribromo phenol.

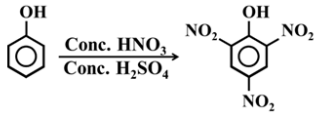


Nitration

Phenol reacts with dil. HNO3 at 0°–10° C to form ortho- and para- nitro phenols.



When phenol is treated with nitrating mixture it forms 2,4,6- trinitro phenol (picric acid).

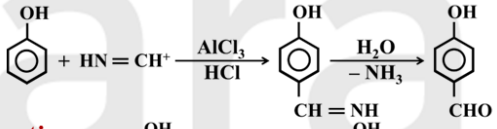


[2, 4, 6–Trinitrophenol (Picric acid)]

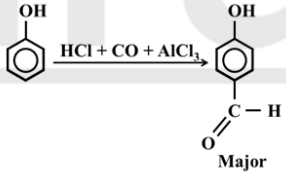
Gattermann Reaction

When Phenol is treated with liquid HCN and HCl gas in presence of anhydrous AlCl3 it yields mainly p- hydroxy benzaldehyde (formylation)

$HCl + HCN \xrightarrow{AlCl_3} HN=CH^+$



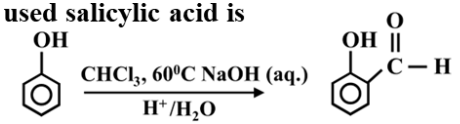
Gatterman Koch Reaction



Reimer-Tiemann Reaction

Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde (As major product).

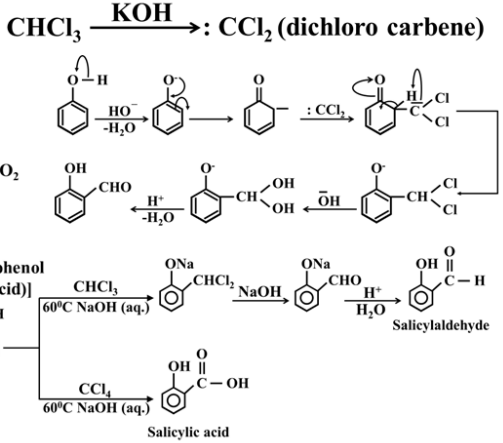
When CCl_4 is used salicylic acid is formed.



Salicylaldehyde

Mechanism

Dichlorocarbene is neutral attacking electrophile (formed by a- elimination reaction)



Kolbe-Schmidt Reaction

This involves the reaction of C_6H_5ONa with CO_2 at 140^0 C followed by acid hydrolysis salicylic acid is formed.

Test of Phenol

(i) Phenol turns blue litmus to red.

(ii) Aqeous solution of phenol gives a violet colour with a drop of $FeCl_3$

(iii) Aqeous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.

$R-OH \xrightarrow[\text{CAN Test}]{\text{Cerric Ammonium Nitrate}} \text{Red / Pink colour}$

Helps to differentiate b/w alcohol and phenol

MIND MAP

Ether and Epoxy

Ether

R– O – R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

$$R-OH \xrightarrow[+R]{-H} R-O-R \xleftarrow[+2R]{-2H} H-O-H$$

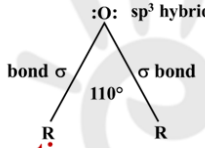
Classification

They may be classified as
(a) Simple or symmetrical ether. e.g. R–O–R
(b) Mixed or unsymmetrical ether e.g. R–O–R'

Structure

The molecule of ether is bent due to lone pair of electron on oxygen atom. The bond angle is 1100.
It is greater than that of water 104.50 due to the repulsion between bulky alkyl groups.

Due to bent structure, it posses dipole moment and hence are polar molecules.



General Methods of Preparation

From Alkyl Halides

(i) By Williamson's synthesis

$$R-X + Na-O-R \longrightarrow R-O-R + NaX$$

[S_N2 Reaction]

$$CH_3-I + C_2H_5O^-Na^+ \longrightarrow CH_3-CH_2O-CH_3 + NaI$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + CH_3ONa \longrightarrow H_3C-\underset{\underset{CH_3}{||}}{\overset{\overset{CH_2}{|}}{C}}$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-ONa + CH_3-CH_2-Cl \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2-Cl$$

Chemical Properties of Ethers

Ethers are less polar so less reactive and do not react with active metals (Na,K) cold dil. acid, oxidising and reducing agent.

They do not have any active functional group.

1. Basic nature

Due to presence of lone pair on oxygen atom ethers behave as lewis base. Ethers react with cold concentrated acid and form oxonium ion

Ethers form dative bond with Lewis Acids like BF3, AlCl3, RMgX etc.

$$C_2H_5\ddot{O}C_2H_5 \xrightarrow{\text{cold ; conc. HCl}} \left[C_2H_5-\overset{\oplus}{\underset{\underset{H}{|}}{O}}-C_2H_5\right]Cl^-$$

(diethyl oxonium chloride)

(i) Reaction with Dry Ag2O

$$2RX + Ag_2O \xrightarrow{\Delta} R-O-R + 2AgX$$

$$2CH_3-CH_2-Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$$

From Alcohol

(i) By dehydration

$$R-OH \xrightarrow[\Delta]{\text{Con. } H_2SO_4} ?$$

$$CH_3-CH_2-OH \xrightarrow{\text{Conc. } H_2SO_4} \begin{cases} \xrightarrow{413K} CH_3CH_2-O-CH_2CH_3 \\ \text{(Williamson's Substitution favored synthesis)} \\ \xrightarrow{443K} CH_2-CH_2 \quad \text{(Elimination)} \\ \text{(Elimination favored)} \end{cases}$$

$$CH_3=CH-Cl + CH_3CH_2-ONa \longrightarrow \text{No reaction}$$

[Stable by Resonance]

Reaction with hot dil. H_2SO_4

$$R-O-R \xrightarrow[H_2SO_4]{\text{hot dil.}} 2R-OH$$

Reaction with PCl_5

$$ROR + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$$

Reaction with HX

Reactivity of HX **HI > HBr > HCl**

Reaction with cold conc. HX
Ethers forms oxonium salt with cold and conc. HCl (less reactive)
Cold conc. HI and HBr (more reactive) break C–O bond.

$$CH_3-O-CH_2-CH_3 \xrightarrow[HI]{\text{Cold and conc.}}$$

If oxonium ion gives more stable carbocation(3° and more stable Carbocation then SN1 mechanism)

$$\left[Ph\overset{\oplus}{C}H_2, CH_2=CH-\overset{\oplus}{C}H_2, (CH_3)_3\overset{\oplus}{C}\right]$$

then S_N1 reaction occurs.

If excess of HI is used then two moles of alkyl hallides are formed.

$$CH_3CH_2-O-CH_2Ph \xrightarrow{HI} CH_3CH_2OH + PhCH_2I$$

$$\downarrow HI$$

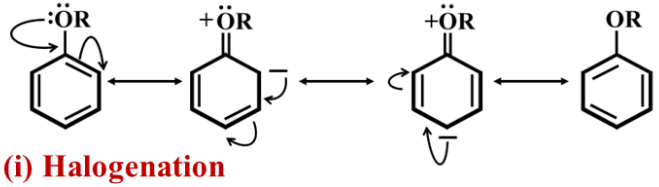
$$CH_3CH_2-I + PhCH_2-I$$

MIND MAP

Ether and Epoxy

Electrophilic Substitution

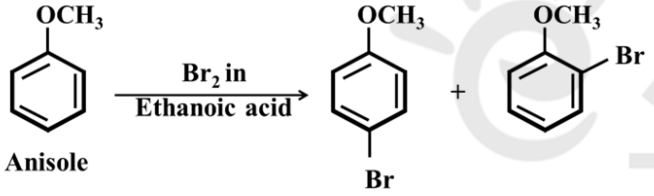
The alkoxy group (-OR) is ortho , para directing and activates the aromatic ring towards electrophilic substitution.



(i) Halogenation

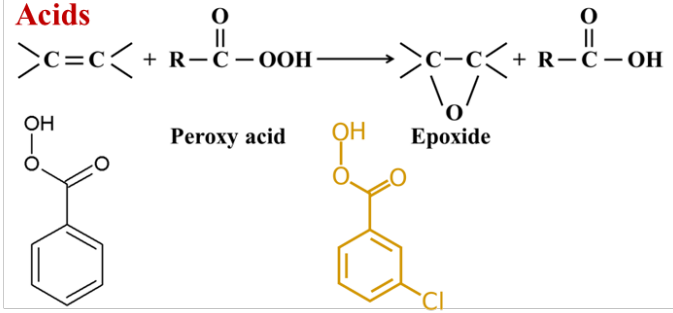
Phenylalkyl ethers undergo usual halogenation in the benzene ring. e.g. anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst.

It is due to the activation of benzene ring by the methoxy group. Para isomer is obtained in 90% yield.

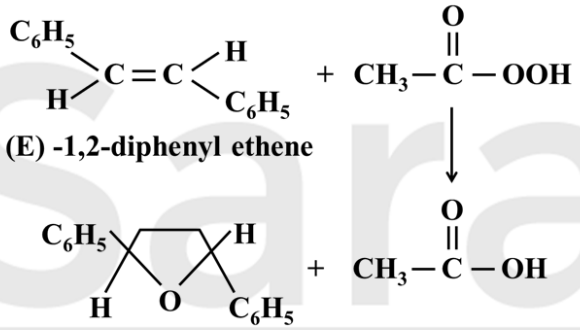


Epoxides

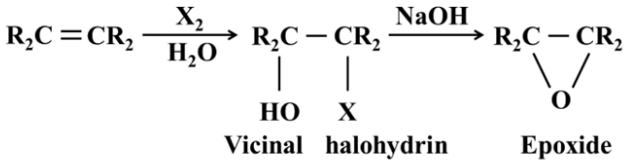
Epoxidation of Alkenes By Reaction With Peroxy Acids



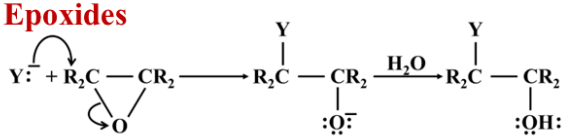
Epoxidation is a stereospecific syn addition



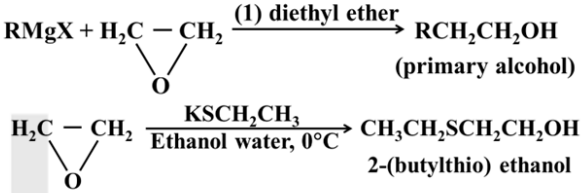
Base-promoted Ring Closure of Vicinal Halohydrins



Nucleophilic Ring Opening Reactions of Epoxides



With Grignard Reagent



Note

Nucleophilic ring opening reactions of epoxides is the characteristic feature of S_N2 reaction.